SOURCE, OCCURRENCE AND MODELING OF PHARMACEUTICALS, PERSONAL CARE PRODUCTS AND ESTROGENS ON THE GYEONGAN RIVER BASIN IN KOREA

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SOURCE, OCCURRENCE AND MODELING OF PHARMACEUTICALS, PERSONAL CARE PRODUCTS AND ESTROGENS ON THE GYEONGAN RIVER BASIN IN KOREA

（韓国Gyeongan川流域での医薬品類とエストロゲン類の排出源、汚染実態とモデルの作成）

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ABSTRACT

Pharmaceuticals and personal care products (PPCPs) and estrogens have been found incompletely removed in various conventional sewage treatment plants (STPs). Wide presence of estrogens and PPCPs in STP effluents and in receiving aquatic environments may affect water quality and pose potential risks to aquatic organisms and human health. Korea is one of the countries using PPCPs extensively. PPCPs are important substances that are essential for treatment of disease as well as for improvement of health. Various types of PPCPs are produced and prescribed globally, and their variety and production quantities are increasing. However there is a growing concern that PPCPs discharged into the environment might cause potentially adverse effects on environment and human health. And more recently, environmental research has increasingly focused on endocrine-disrupting chemicals (EDCs), which have proven to cause fertility reduction, feminization and other adverse effects in male animals within natural and laboratory settings. The most concerned and studied hormones are steroid estrogens, including natural steroid estrogens which are primarily excreted by humans and animals, e.g. estrone (E1), 17β-estradiol (E2), estriol (E3), and synthetic steroid estrogens which are used as oral contraceptives, mainly ethinylestradiol (EE2). Natural and synthetic estrogens are excreted by human bodies and reach the aquatic environment daily via sewage systems. Research on the effects of estrogens is increasingly reported in the world, and awareness on the toxicity and danger of estrogens is rising. The final aim of this study is to recognize PPCPs, estrogens and veterinary pharmaceuticals (VPs) detected from Korea and look into their behavior at STPs and the river as well as removal characteristics by treatment process. It also aims to build a model for estimating the predicted concentration of PPCPs and estrogens remaining in the effluent of the STPs and the river and to evaluate and propose effective management of the river basin.

Firstly, the characteristics of PPCPs and estrogens detected in Korean STPs and the removal efficiencies by different biological treatment and various disinfections were compared. STPs

using the modified Ludzack-Ettinger (MLE) process, anaerobic anoxic aerobic (A2O) process, conventional activated sludge (CAS) process and Bio Best Bacillus (B3) process were selected. In the comparison of the removal efficiencies of the biological treatments of the STPs, the MLE and A2O processes were found to be more efficient than the CAS process in management PPCPs effectively. And ozone treatment used as disinfection process at a STP studied is for the purpose of disinfection, showed relatively lower removal efficiency of PPCPs and estrogens showed lower efficiency than the existing reports. Besides, for effective control of PPCPs and estrogens, we can put solids retention time (STR) at over 7-10 days and increase the efficiency in removing bezafibrate, naproxen, estrone and levofloxacin.

Second, the study will grasp the removal characteristics and behavior of residual VPs in a STP treating both the livestock wastewater and domestic wastewater introduced in the treatment plant. The VPs detected chiefly in the STP include tiamulin, chlortetracycline, sulfadimethoxine and thiamphenicol while pharmaceuticals used by both animals and humans were found to be enrofloxacin, estrone, oxytetracycline, tylosin and sulfadimidine. There were 51 kinds of PPCPs contained in dewatering sludge, which included large amounts of VPs as well as levofloxacin, tiamulin and sulpiride. Then, for the entire process of STPs, removal efficiency of PPCPs and estrogens were compared with that in consideration of sludge adsorption. While compounds such as roxithromycin, propranolol, levofloxacin and disopyramide are adsorbed on sludge, metoprolol, sufamerazine and triclocarban showed a small amount of sludge adsorption. Tiamulin detected from livestock wastewater showed tendency to be absorbed in sludge while chlortetracycline, sulfadimethoxine and thiamphenicol are being removed from the biological treatment.

Third, the study is to appreciate seasonal characteristics of water pollution and main substances with analysis on concentrations of PPCPs and estrogens inflowing to Gyeongan River. PPCPs and estrogens that show the high composition in the influent of STPs in Korea are antibiotics and non-steroidal anti-inflammatory drugs (NSAIDs). For PPCPs and estrogens by season, antipyrine,

crotamiton, DEET, ethenzamide, primidone and sulfadimidine were detected in the summer in high concentration while in the winter acetaminophen, bezafibrate, chlortetracycline, fenoprofen, norfloxacin, sulpiride, tetracycline, thiamphenicol and tiamulin were characteristically detected in high concentration.

Forth, primary aim of this modeling was to predict the concentrations of frequently detected PPCPs and estrogens in a Gyeongan River basin using the model. Additional aim is to propose effective basin management by enhancing the model so that it may suit PPCPs and estrogens. To install the factors of model, this research conducted experiments of photolysis, biodegradation and absorption on the subject of Gyeongan River. In photolytic experiment, a total of 28 substances, including 8 substances of NSAIDs, 15 of antibiotics and the other 5, showed a decay rate over 10 %. Biodegradation was conducted in division into upstream and downstream and the latter showed higher decay rates. PPCPs and estrogens with a decay rate over 10 % were sorted into 22 compounds. Other substances were under 10 % of decay rate, which was considered to have a low contribution to biodegradation. Lastly, since absorption mostly showed a low decay rate of adsorption, this study assumed that there is no river-line decay of PPCPs and estrogens studied caused by adsorption. There are limitations in this experiment: Since it was the verification of adsorption by in-vitro with a simple revolution where there was no water flow, it is not certain whether this is actually adsorbed in the river. Besides, since there are diverse particles and substances in the river, we cannot exactly assume that PPCPs and estrogens are adsorbed as the adsorption experiment above. As a result of applying the model on the target of Gyeongan River, PPCPs and estrogens between measurement and estimation of loading show a high degree of agreement.

Finally, Chapter 7 combined the loadings of PPCPs and estrogens effluent to the river from STPs and small-sized facilities earned from Chapter 3 and 4, with the model of estimated water quality in the river from Chapter 6 to estimate the concentration of water quality for PPSPs and estrogens in Gyeongan River. Besides, we proposed measures in sewage treatment process for

reducing the pollution of PPCPs and estrogens at Gyeongan River, earned from Chapter 5, and reviewed the effect. The result showed that concentrations of PPCPs and estrogens measured at Gyeongan River almost corresponded to the estimates in the model. At Gyeongan River, besides effluent from STP, PPCPs and estrogens in small-sized sewage facilities at the uppermost basin and upstream area of the tributary become a large source of loadings, so we established diverse scenarios for countermeasure. We improved biological method of STP at Gyeongan River into A2O process and the existing chlorine disinfection into UV disinfection. Despite this improvement with the existing A2O process and UV disinfection, it was not sufficient to lower ecological toxicity. Therefore, we introduced ozone treatment and UV treatment with the purpose of removing PPCPs and estrogens while performing UV and ozone treatments on small-sized STP with poor management of water quality. However, the result was not enough simply by adding biological and ozone treatments to STPs located at Gyeongan River, for it was impossible to reduce the biological toxicity of clarithromycin with the highest hazard quotient (HQ) among substances detected from Gyeongan River. Still, we were able to lower the river's HQ by managing both small-sized STPs and Gyeongan River's together. Particularly, executing ozone treatment of 4 mg/L proved to lower HQ below 0.1 for all substances and for all seasons.

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LIST OF ABBREVIATIONS

ACT: Acetaminophen
2QCA: 2QCA
ANP: Antipyrine
ATL: Atenolol
AZI: Azithromycin
BZF: Bezafibrate
CAF: Caffeine
CMZ: Carbamazepine
CF: Ceftiofur
CTC: Chlortetracycline
CIPX: Ciprofloxacin
CLA: Clarithromycin
CLB: Clenbuterol
CFA: Clofibric_acid
CRT: Crotamiton
DEET: DEET
DCF: Diclofenac
DTZ: Diltiazem
DIP: Dipyridamole
DIS: Disopyramide
ENR: Enrofloxacin
ERY: Erythromycin
ERYH: Erythromycin-H2O
E2: Estradiol
E3: Estriol
E1: Estrone
ETZ: Ethenzamide
EE2: Ethynylestradiol
FPF: Fenoprofen
FUR: Furosemide
GF: Griseofulvin
IBU: Ibuprofen
IFP: Ifenprodil
IND: Indometacin
IPA: Isopropylantipyrine
KTP: Ketoprofen
LVF: Levofloxacin
LCM: Lincomycin
MEF: Mefenamic_acid
MTL: Metoprolol
NDA: Nalidixic_acid
NAP: Naproxen
NFX: Norfloxacin
OXT: Oxytetracycline
PIR: Pirenzepine
PRI: Primidone
PPL:Propranolol
ROX: Roxithromycin
SAL: Salbutamol
SDMX: Sulfadimethoxine
SDM: Sulfadimidine
SMR: Sulfamerazine
SMZ: Sulfamethoxazole
SMM: Sulfamonomethoxine
SP : Sulfapyridine
STZ: Sulfathiazole
SLP: Sulpiride
TC: Tetracycline
TPL: Theophylline
TAP: Thiamphenicol
TL: Tiamulin
TCC: Triclocarban
TRI: Triclosan
TMP: Trimethoprim
TYL: Tylosin

CHAPTER I

INTRODUCTION

1.1 Research background

Pharmaceuticals and personal care products (PPCPs) are indispensable for curing those who suffer from disease and their availability improves the quality of life (Brausch et al., 2012; Daughton and Ternes, 1999; Heberer, T et al., 1997; Jones et al., 2001; Stackelberg et al., 2004). Veterinary pharmaceuticals (VPs) are also widely used to treat disease and improve the productivity of livestock farming (Boxall et al., 2002; Halling-Sørensen et al., 2002). However, during their use, human and veterinary pharmaceuticals have the potential of being released into the environment. In recent years, the possible environmental risk of PPCPs and estrogens in the aquatic environment has become a matter of increasing public concern (Barcelo D et al., 2008; Caliman et al., 2009; Caserta et al., 2008; Goldman et al., 2000; Kreisber J, 2007). PPCPs and estrogens are introduced into the environment through various routes. Generally they enter the environment during manufacture or after use by both humans and animals; ① release from PPCPs manufacturing facilities, ② disposal of unused PPCPs by patients, hospitals, or distributors either to wastewater or to solid waste, or ③ patient excretion of PPCPs, estrogens and their metabolites to wastewater. Human wastes are typically treated in sewage treatment plants (STPs). During the treatment, PPCPs may be degraded via hydrolysis, oxidation, or biodegradation, or the PPCPs may adsorb to solids that are isolated in sludge. Concentrations of PPCPs in STP effluents depend on the removal efficiency of the STP treatment processes (Ilho, Kim et al., 2009). STP effluents are generally considered the primary source of human PPCPs into the aquatic environment. In addition, a STP release untreated wastewater during a storm event or a potential transportation accident could be non-routine episodes that admit additional discharge of PPCPs into the environment (William, 2005). VPs, used for farming, are characterized by leaking out through diverse channels. VPs may pose more threat to ecosystems than human PPCPs because of their characteristics of environmental release (Park et al., 2007). When they are used in agriculture field or excreted directly on land, VPs are released directly into the environment if they are discharged without any appropriate treatment and/or storage. They also indirectly enter into the environment when manure containing excreted VPs are applied onto land. Since VPs are typically nonpoint source pollutants, it is more difficult to effectively manage their contamination compared to human pharmaceutical contamination. Once released into the environment, VPs and their metabolites have the potential to run off directly into surface waters (Focazio et al., 2008) or leach into groundwater (Barnes et al., 2008). Next, estrogens are a group of compounds named for their importance in both menstrual and estrous reproductive cycles. The human and veterinary population and related STPs are considered to be the main pollution source of these chemicals in the aquatic environment. When estrogen contaminated water is released into

streams, the most pronounced effect is occurring with aquatic species that make their homes in waters with elevated levels of estrogens. These generally occur downstream from STPs. Fish in these areas worldwide are being feminized (Yan Zheng 1998).

Since PPCPs are used diversely, their pathways of exposure to environment are also diverse and hard to predict. In addition, identification and detection of PPCPs and estrogens in the aquatic environment requires highly sensitive instruments that consume considerable endeavor, time and money. There are two GIS-based models used for prediction of the predicted environmental concentration for PPCPs and estrogens in the environment. PhATE (Pharmaceutical Assessment and Transport Evaluation) much used in the US was developed by PRMA (Pharmaceutical Research and Manufacturers of America) as an instrument for evaluating the concentrations of active medical substances (Anderson et al., 2004). Similarly, GREAT-ER (Geography-referenced Regional Exposure Assessment Tool for European Rivers) was developed as a means to predicting the concentration of water chemicals and finding the distribution of concentration of such compounds at the surface water in Europe (Schowanek and Webb, 2002). These models can be used to estimate the potential risk of chemicals in the aquatic environment. Each river has different conditions in microorganisms, sunshine and earth. Thus, this modeling is going to build a model suited for Gyeongan River in Korea.

1.2 Research objectives

According to the above research background, detailed objectives of this research are as follows;

1) This evaluates the concentrations of PPCPs and estrogens detected from Korean rivers and STP by season. Then, it verifies the characteristics and occurrences of PPCPs and estrogens appearing in influent, secondary effluent, final effluent and river and their removal characteristics.
2) To grasp kinds of VPs chiefly used in Korea and their behavior in the river. Then, understand their characteristics of being removed from STPs. Then, grasp the removal characteristics from STPs and propose the management of the study on VPs.
3) To monitor and evaluate environmental risk on PPCPs and estrogens detected from rivers in Korea.
4) To evaluate factors (photolysis & biodegradation) needed for a model to predict PPCPs and estrogens.
5) To predict PPCPs and estrogens in the target river using model with identified factor and to evaluated countermeasures.

The objective of this modeling was to predict the concentrations of frequently detected PPCPs and estrogens on a watershed using the model in Korea.

1.3 Research structure

This dissertation consists of nine chapters. Figure 1.1 shows the schematic diagram of research and dissertation structure. Introduction of each chapter is as follows; In Chapter I, research

background, research objectives and research structure were described.

In Chapter II, literature review presenting brief introduction of PPCPs, estrogens and overview of scientific knowledge of their occurrence, fate and removal characteristic in river and STPs are described.

In Chapter III, the characteristics of PPCPs and estrogens detected in Korean STPs and the removal efficiencies by different biological treatment and chemical treatment of various disinfections were compared.

In Chapter IV, though VPs are used for protecting or treating humans from disease, problems of generating resistance to PPCPs for microbes are reported in many countries in relation to their abuse and misuse. This chapter will grasp the removal characteristics and behavior of residual VPs in the livestock wastewater and domestic wastewater introduced in the treatment plant. Then through understanding problems of the STP located in the region of study, the researcher will seek for the way to manage the VPs.

In Chapter V, this chapter is to appreciate seasonal characteristics of water pollution and main substances with analysis of PPCPs and estrogens inflowing to Gyeongan River. Gyeongan River locating around the metropolitan area continuously experiences land utilization changes and expects pollutants increase following development.

In Chapter VI, model of this study was built for the efficient management of PPCPs and estrogens and the exact evaluation on concentrations. The final aim of this modeling was to predict the concentrations of frequently detected PPCPs and estrogens on the Gyeongan River basin using the model. Additional aim is to propose effective basin management by enhancing the model so that it may suit PPCPs and estrogens. Thus, this chapter aims to compose a model and install reduction factors for building a model. Installing factors influences the change in PPCPs and estrogens and is an important element for an estimation model. This chapter considered 61 kinds of PPCPs and 4 kinds of estrogens by photolysis, biodegradation and adsorption at Gyeongan River.

In Chapter VII, the constructed model was applied to Gyeongan River basin to predict the occurrence and concentrations of PPCPs and estrogens. PPCPs and estrogens remaining in effluent are imported in the river and exposed to environment. To manage such Gyeongan River, we proposed a method of reducing PPCPs and estrogens influent to Paldang Lake by adding ozone process to diverse STPs.

In Chapter VIII, conclusions from this research and recommendations for the further research were summarized.

This study presented:

1. The basis of the abuse and misuse of PPCPs used for human and animal leading to leakage to river and adverse effect and verified the PPCPs and estrogens discharged from STP and livestock wastewater treatment plant without treatment.

2. Centering on PPCPs and estrogens that can make harmful effect on ecosystem and humans.

3. This is an important study that describes their inflow, outflow, kinds, behavior, estimation, present situation of contamination and management in STP and river to present the direction and content of future research.

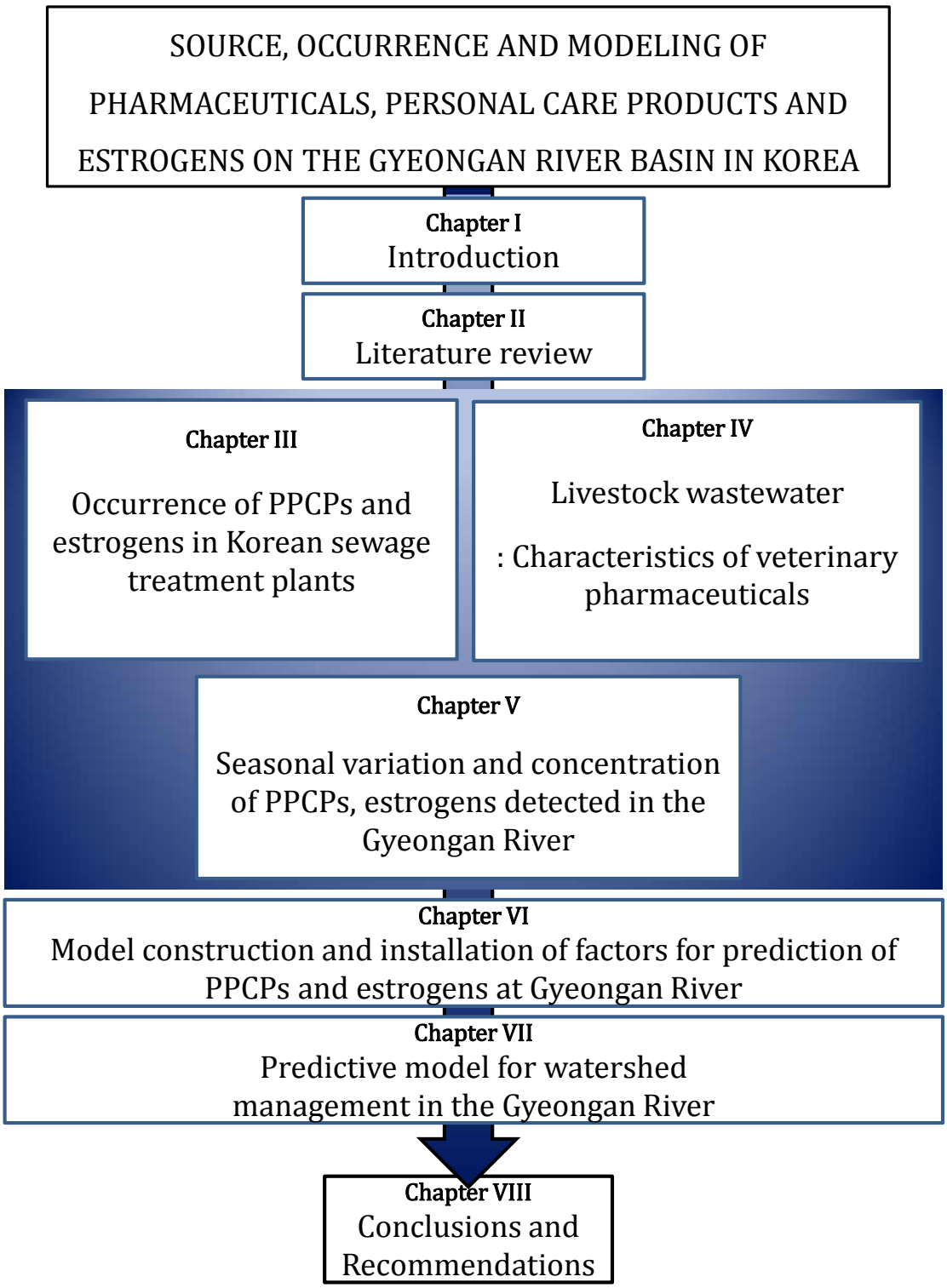

Figure 1.1 Schematic diagram of research and dissertation structure

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CHAPTER II

LITERATURE REVIEW

2.1 Introduction

Pharmaceuticals and personal care products (PPCPs), estrogens which contain diverse organic groups, such as antibiotics, hormones, synthetic musks, etc., have raised significant concerns in recently years for their persistent exposure and potential threat to ecological environment and human health (Carballa et al., 2004; Daughton and Ternes, 1999; Kummerer, 2000). Humans ingest PPCPs and related products almost daily, and a certain fraction of each dosage is excreted due to incomplete metabolism in the human body. This excreted fraction ultimately discharges to surface waters as anthropogenic wastewater (Radjenovic et al., 2008; Ternes et al., 2002; Vieno et al., 2007a; Glassmeyer et al., 2008; Harries et al., 1996; Desbrow et al., 1998; Johnson et al., 2000; Komori et al., 2004; Gentili et al., 2002; Reddy et al., 2005). Consequently, PPCPs and estrogens are discharged to the environment in both unaltered parental and metabolized forms. Overall, sewage treatment plants (STPs) are the single largest source of PPCPs and estrogens loading into surface waters (Barnes et al., 2008; Focazio et al., 2008). PPCPs and estrogens pass through a given STP, a certain amount of removal occurs via the combined processes of biodegradation, mineralization, adsorption, photolysis, and volatilization. After discharge into surface waters, the relative influence of the various attenuation processes is not completely understood and is subject to site-specific conditions. Furthermore, the influence and mechanisms for sorption of PPCPs and estrogens in surface water is at present unclear (Bendz, D. et al., 2005; Moldovan, Z. et al., 2006; Kim, S. D. et al., 2007). In general, these hydrophilic compounds will remain in the aqueous phase and are not likely to have high sorption capacities (Stumpf, M et al., 1999; Kolpin, D. W et al., 2002; Calamari, D. et al., 2003). However, hydrophobic partitioning is not the only critical factor in PPCPs sorption - other mechanisms, such as ion exchange, hydrogen bonding, and mineral adsorption, can also play a significant role (Stumpf, M et al., 1999).

2.2 Pharmaceuticals and personal care products and estrogens

2.2.1 Emerging environmental pollutants

Emerging environmental pollutants, pharmaceuticals and personal care products (PPCPs), and estrogens have attracted much public attention. Increasing numbers of water samples obtained from lakes, streams, aquifers and municipal supplies across the world have been found to be contaminated by trace quantities of such residues (Vimal K. et al., 2009; Wu and Janssen, 2011; Brausch and Rand, 2011; Basile et al., 2011). The treated effluents of STPs that were discharged into surface water bodies could be an important sources for PPCPs and estrogens to enter the

aquatic environment, and the fate, transport and potential adverse effects on aquatic biota have been delineated (Boxall et al., 2012; Kleywegt et al., 2011; Boleda et al., 2011; Abdelmelek et al., 2011). During the sewage treatment, the PPCPs residues may be adsorbed by the mixed liquor suspended solids and subsequently removed from water stream by sedimentation (Jelic et al., 2011). Municipal wastewater sludge, the solid fractions separated from the wastewater stream, therefore is potentially a sink of the wastewater-borne PPCPs (Bikram S. et al., 2014; Motoyama et al., 2011). The publicly-owned sewage treatment works in the U.S. generate over 8 million tons (dry weight) of wastewater sludge annually, about 41% was applied to land and 17 % were landfilled, are potential sources of PPCPs and EDCs in the terrestrial environment and in groundwater (EPA 832-R-06-005, 2006).

2.2.2 Classification of pharmaceuticals and personal care products

PPCPs contain diverse groups of organic compounds, such as antibiotics, hormones, anti-inflammatory pharmaceuticals, antiepileptic pharmaceuticals, blood lipid regulators, β-blockers, contrast media, and cytostatic pharmaceuticals for pharmaceuticals; and antimicrobial agents, synthetic musks, insect repellants, preservatives, and sunscreen UV filters for personal care products (Table 2.1) (Daughton and Ternes, 1999; Mompelat, S. et al., 2009).

Table 2.1 Classification of PPCPs and estrogens

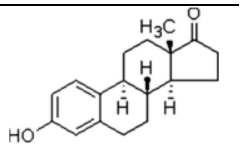
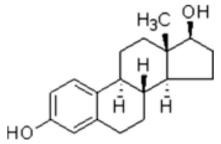
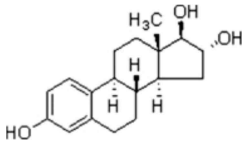
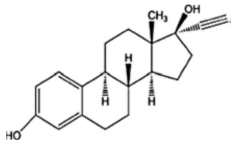
	Subgroups	Representative compounds	Abbreviations
Pharmaceuticals	Antibiotics	Clarithromycin	CLA
		Erythromycin	ERY
		Sulfamethoxazole	SMZ
		Sulfadimethoxine	SDMX
		Ciprofloxacin	CIPX
		Norfloxacin	NFX
		Chloramphenicol	
	Hormones	Estrone	E1
		17β -Estradiol	E2
		Ethinylestradiol	EE2
	Analgesics and anti-inflammatory pharmaceuticals	Diclofenac	DCF
		Ibuprofen	IBU
		Acetaminophen	ACT
		Acetylsalicylic acid	
	Antiepileptic pharmaceuticals	Carbamazepine	CMZ
		Primidone	PRI
	Blood lipid regulators	Clofibrate	
		Gemfibrozil	
	β-blockers	Metoprolol	MTL
		Propanolol	PPL
	Contrast media	Diatrizoate	
		Iopromide	
	Cytostatic pharmaceuticals	Ifosfamide	
		Cyclophosphamide	
Personal Care Products	Antimicrobial agents/Disinfectants	Triclosan	TRI
		Triclocarban	TCC
	Synthetic musks/Fragrances	Galaxolide	HHCB
		Toxalide	AHTN
	Insect repellants	N,N-diethyl-m-toluamide	DEET
	Preservatives	Parabens (alkyl-p-hydroxybenzoates)	
	Sunscreen UV filters	2-ethyl-hexyl-4-trimethoxycinnamate	EHMC
		4-methyl-benzilidine-camphor	4MBC

Among the pharmaceutical group, antibiotics have received special attention for their wide application in human therapy and livestock agriculture. Persistent exposure of antibiotics can result in the emergence of resistant bacteria strains with public health concerns (Zhang et al., 2009b). Antibiotics contain several subgroups, such as macrolides, sulfonamides, and fluoroquinolones.

2.2.3 Definition of estrogens

The most concerned and studied hormones are steroid estrogens, including natural steroid estrogens which are primarily excreted by humans and animals, e.g. estrone (E1), 17β-estradiol (E2), estriol (E3), and synthetic steroid estrogens which are used as oral contraceptives, mainly ethinylestradiol (EE2) (Desbrow et al., 1998; Hanselman et al., 2003; Zheng et al., 2008). Physicochemical properties of the 4 compounds are shown in the Table 2.2 (Ying et al., 2002; Petrovic and Barceló 2007).

Table 2.2 Physicochemical properties and structures of estrogens E1, E2, E3 and EE2

Estrogen	Mol. wt. (g mol^{-1})	SW (mg L^{-1}, at 20 ℃)	Vapour pressure (mm Hg)	Sorption constant, K_{oc}	Henry's Law constant (atm m^3 mol^{-1})	Log K_{ow}	Structure
Estrone (E1)	270.4	13	2.3 X 10^{-10}	4882	3.80 X 10^{-10}	3.43	
17β - Estradiol(E2)	272.4	13	2.3 X 10^{-10}	3300	3.64 X 10^{-11}	3.94	
Estriol (E3)	288.4	13	6.7 X 10^{-15}	1944	1.33 X 10^{-12}	2.81	
17α- Ethinylestradiol (EE2)	296.4	4.8	4.5 X 10^{-11}	4770	7.94 X 10^{-12}	4.15	

2.3 Occurrence of PPCPs and estrogens in Korea

2.3.1 Detection of PPCPs in Korea

PPCPs are divided into substances used by humans, animals, and humans and animals together. This 2.3.1 investigated Korean research papers dealing with PPCPs used by humans. The presence of PPCPs in Korea surface waters or wastewater treatment has been observed by a number of researchers (Choi, K. et al., 2008; Kim S.D. et al., 2007). In the STP influents, acetaminophen (6.80 ± 2.41 mg/L), acetylsalicylic acid (6.29 ± 3.39 mg/L) and caffeine (3.37 ± 1.94 mg/L) were the most dominant. The levels in the STP influents are related to the production and consumption of PPCPs in Korea. PPCPs in the hospital STP influent showed a higher concentration (5 – 12 times) than those in the STP influent samples, with caffeine (56.1 mg/L), ciprofloxacin (45.0 mg/L) and acetaminophen (41.9 mg/L) being dominant. In the rivers, caffeine (0.260 ± 0.254 mg/L) showed a relatively high concentration (Choi, K. et al., 2008). In the receiving water of the STPs, the distribution patterns of PPCPs are similar to those in the STP effluents. Several PPCPs (e.g., acetaminophen, caffeine, acetylsalicylic acid, ibuprofen, gemfibrozil, ketoprofen and naproxen) showed significant concentration decrease rates in the STPs, and they are decreased mainly by the biological treatment processes (National Institute of Environmental Research of Korea. 2006; Choi, K. et al., 2008; Kim, S. D. et al., 2007). In the physico-chemical processes of the STPs, some PPCPs showed significant decrease rates, and the results of sand filtration were the most significant among them. In the hospital STP, the decrease rates of ciprofloxacin, acetylsalicylic acid, acetaminophen and carbamazepine were relatively high (over 80%). Although the decrease efficiencies of several PPCPs were significant in

the STPs and hospital STP, their removal in the wastewater treatment processes needs to be studied and improved to manage all the pharmaceuticals found in the sources effectively (Kim, S. D. et al., 2007). In the rivers, 10 compounds were detected out of 25 target PPCPs, with the total concentrations ranging from 0.061 to 0.717 mg/L (0.416 ± 0.258 mg/L). Unlike the results of the STPs, caffeine had the highest concentrations (0.260 ± 0.220 mg/L) in the rivers. Erythromycin-H2O (0.072 ± 0.049 mg/L), acetylsalicylic acid (0.054 ± 0.048 mg/L), acetaminophen (0.047 ± 0.029 mg/L), ibuprofen (0.040 ± 0.011 mg/L), carbamazepine (0.037 ± 0.030 mg/L), lincomycin (0.034 ± 0.022 mg/L), mefenamic acid (0.018 ± 0.013 mg/L), naproxen (0.012 ± 0.001 mg/L) and clofibric acid (0.009 ± 0.005 mg/L) were also detected in the river water samples (National Institute of Environmental Research of Korea. 2006; Choi, K. et al., 2008; Kim S.D. et al., 2007). Among these PPCPs, caffeine, carbamazepine and acetylsalicylic acid showed a high frequency of detection (Choi, K. et al., 2008; Kim, S. D. et al., 2007). Especially, acetylsalicylic acid, acetaminophen and caffeine, which are the dominant compounds in the STP influents, often showed higher concentrations than those in the STP effluents. This suggests the possibility of untreated wastewater flowing into the rivers. As the percent of sewered population (the percentage of the population living in sewer service area among the total population) in the target region is 74.5 % according to an environmental annual report (Ministry of Environment of Korea, 2008), some raw wastewater might have gone directly into the rivers.

2.3.2 Detection of estrogens in Korea

Previously, there were several studies in Korea that reported the occurrence and distribution of trace pollutants including estrogens (Khim et al., 1999; Li. D.H. et al., 2004a; Li. Z.Y. et al., 2004b; Oh et al., 2006). Samples were collected to investigate the occurrence of estrogens from surface waters in Yeongsan River and Seomjin River, Korea and influents and effluents of STPs adjacent to the rivers. The EEQ (estradiol equivalent) concentrations of estrogenic chemicals may be varied according to the estradiol equivalent factor (EEF) obtained from different assays. The average concentrations of estrogens (expressed as estradiol equivalent – EEQ) in surface waters were estimated to be as high as 3.8, 6.3, and 5.9 ng L^{-1} for the years 2005, 2006 and 2007, respectively (Khim et al., 1999). There was no significant difference ($p > 0.05$ in ANOVA) in the average EEQ of surface water between these 3 years. The average EEQ concentrations of influents of investigated STPs (i.e., 23, 33.9 and 24.2 ng L^{-1} for 2005, 2006 and 2007, respectively) were significantly different from those of surface waters and effluents. This indicated that treatment processes of STPs remarkably reduced the estrogenic activity of estrogenic compounds before being discharged into river waters. However, the average EEQ concentrations of surface water estimated in 2005 and 2006 were significantly ($p < 0.05$) higher than those detected in the effluents of STPs (i.e., 0.29 and 0.1 ng L^{-1} for 2005 and 2006, respectively). It is noted that there may be other sources of estrogenic compounds being introduced into these rivers other than the effluents of STPs. However, the average EEQ concentration in STP effluents collected in 2007, which was estimated to be as high as 4.9 ng L^{-1}, was significantly higher ($p < 0.05$) than those collected in 2005 and 2006 (Kim et al., 1999).

2.3.3 Comparison of the concentration of PPCPs and estrogens in Korea and the other countries

Present condition of PPCPs detection for each country of the world was investigated to understand Korea's present state of contamination in comparison. Figure 2.1 and Table 2.3 show the maximum concentration of PPCPs remaining in the influent of STPs in diverse countries. A comparison between detected concentrations of PPCPs in the influents of STPs around the world and that in Korea. Atenolol, ibuprofen, mefenamic acid and naproxen show higher concentrations in Korean STPs than in other countries. Clofibric acid has been detected at the highest concentrations of 740 ng/L in Ireland, and diclofenac has been detected in high concentrations of 4,114 ng/L in Austria. Ibuprofen has been detected at the highest concentrations of 16,500 ng/L in Canada, and ketoprofen has been detected at the highest concentrations of 2,100 ng/L in Spain. Concentrations of PPCPs detected from STP in Korea mostly proved to be high with their likely increase for the future. This suggests a need for the inflow, estimation and treatment of PPCPs and estrogens generated in Korea.

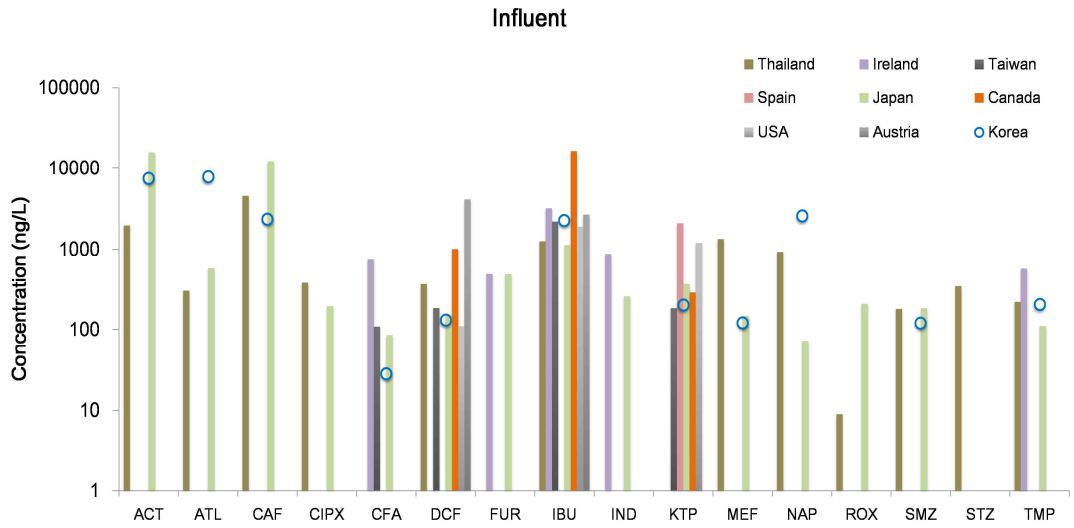


Figure 2.1 Comparison of the concentration of PPCPs and estrogens in influent between STPs in each country of the world and Korea (Seoul)

Table 2.3 Summary of PPCPs and estrogens occurrence in influent in the world

Therapeutic use		Compounds	Abbreviation	Nation [detected concentration (ng/L)]	Ref.
Beta-blocker		Atenolol	ATL	Thailand 304, Japan 579, Korea 7801	S. Tewari et al., 2013, Narumiya et al., 2009 Shishir Kumar Behera et al., 2011
Psycho-stimulant		Caffeine	CAF	Thailand 4550, Japan 12300, Korea 2349	S. Tewari et al., 2013, Narumiya et al., 2009, Sim WJ et al 2010
BLLAs	Fibrate	Clofibric_acid	CFA	Ireland 740, Taiwan 109, Japan 85.4	Lacey, C. et al., 2008, Narumiya et al., 2009
NSAIDs		Acetaminophen	ACT	Thailand 970, Japan 15900, Korea 7460	S. Tewari et al., 2013, Narumiya et al., 2009, Shishir Kumar Behera et al., 2011
		Diclofenac	DCF	Thailand 367, Taiwan 185, Canada 1010, Spain 280, USA 110, Austria 4114, Japan 151, Korea 131	S. Tewari et al., 2013, Gao P. et al., 2012, Robert Loos et al., 2013, Narumiya et al., 2009
		Ibuprofen	IBU	Thailand 1260, Ireland 3204, Taiwan 2200, Japan 1130, Canada 16500, USA 1900, Austria 2679, Korea 2265	S. Tewari et al., 2013, Gao P. et al., 2012, Lacey, C. et al., 2008, Robert Loos et al., 2013, Shishir Kumar Behera et al., 2011
		Indometacin	IND	Ireland 877, Japan 258	Lacey, C. et al., 2008, Narumiya et al., 2009
		Ketoprofen	KTP	Taiwan 184, Spain 2100, Japan 369, Canada 289, USA 1200, Korea 202	S. Tewari et al., 2013, Gao P. et al., 2012, Sim WJ et al 2010
		Mefenamic_acid	MEF	Thailand 1340, Japan 148, Korea 121	S. Tewari et al., 2013, Narumiya et al., 2009, Sim WJ et al 2010
		Naproxen	NAP	Thailand 933, Japan 72.1, Korea 2584	S. Tewari et al., 2013, Narumiya et al., 2009, Shishir Kumar Behera et al., 2011
Antibiotic	Macrolides	Roxithromycin	ROX	Thailand 9, Japan 209	S. Tewari et al., 2013, Narumiya et al., 2009
	Sulfonamides	Sulfamethoxazole	SMZ	Thailand 180, Japan 184, Korea 120	S. Tewari et al., 2013, Narumiya et al., 2009, Shishir Kumar Behera et al., 2011
	Sulfonamides	Sulfathiazole	STZ	Thailand 346	S. Tewari et al., 2013
	Pyrimidines	Trimethoprim	TMP	Thailand 221, Ireland 570, Japan 111, Korea 205	S. Tewari et al., 2013, Lacey, C. et al., 2008, Narumiya et al., 2009, Sim WJ et al 2010
	Fluoroquinolones / Quninolones	Ciprofloxacin	CIPX	Thailand 382, Japan 195	S. Tewari et al., 2013, Narumiya et al., 2009
Diuretic		Furosemide	FUR	Ireland 490, Japan 488	Lacey, C. et al., 2008, Narumiya et al., 2009

Figure 2.2 and Table 2.4 shows the result of PPCPs and estrogens detected from effluents of STP in diverse countries. This compared the maximum concentration of PPCPs and estrogens between papers reported from diverse countries and from STPs in Korea. Atenolol has been detected at the highest concentrations of 934 ng/L in UK, and carbamazepine has been detected in high concentrations of 832 ng/L in EU. Ibuprofen has been detected at the highest concentrations of 460 ng/L in UK, metoprolol has been detected at the highest concentrations of 410 ng/L in UK, and sulfamethoxazole has been detected at the highest concentrations of 910 ng/L in UK. Among the PPCPs remaining in the effluents in Korea, the highest in concentration was lincomycin (1437 ng/L) and triclosan (112 ng/L).

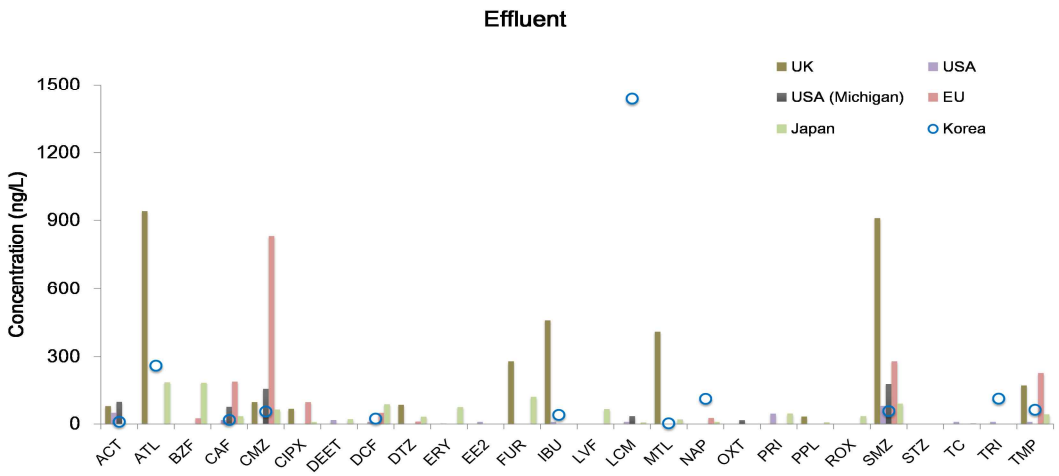


Figure 2.2 Comparison of the concentration of PPCPs and estrogens in effluent from STPs in UK, USA, USA (Michigan), EU and Japan and in Korea

Table 2.4 Summary of PPCPs and estrogens occurrence in effluent in the world

Therapeutic use		Compounds	Abbreviation	Nation [detected concentration (ng/L)]	Ref.
Beta-blocker		Atenolol	ATL	UK 940, Japan 188, Korea 261	Mitchell S. et al., 2014, Xin Yang et al., 2011, Narumiya et al., 2009, Shishir Kumar Behera et al., 2011
		Metoprolol	MTL	UK 410, Japan 20.4, Korea 3	Mitchell S. et al., 2014, Narumiya et al., 2009 Shishir Kumar Behera et al., 2011
		Propranolol	BZF	UK 33, Japan 7.83	Mitchell S. et al., 2014, Narumiya et al., 2009
Psycho-stimulant		Caffeine	CAF	USA 17, USA(Michigan) 76, EU 191, Japan 34.3, Korea 18	Lacey, C. et al., 2008, Robert Loos et al., 2013 , Narumiya et al., 2009, Sim WJ et al 2010
BLLAs	Fibrate	Bezafibrate	BZF	EU 25.4, Japan 186	Robert Loos et al., 2013, Xin Yang et al., 2011 , Narumiya et al., 2009
NSAIDs		Acetaminophen	ACT	UK 79, USA(Michigan) 98, Korea 10	Mitchell S. et al., 2014, Sim WJ et al 2010
		Diclofenac	DCF	USA 10, EU 49.5, Japan 87.4, Korea 24	Lacey, C. et al., 2008, Robert Loos et al., 2013, Mitchell S. et al., 2014, Sim WJ et al 2010
		Ibuprofen	IBU	UK 460, Japan <LOQ, Korea 40	Mitchell S. et al., 2014, Narumiya et al., 2009, Shishir Kumar Behera et al., 2011
		Naproxen	NAP	EU 26.7, Japan 9.47, Korea 111	Robert Loos et al., 2013, Narumiya et al., 2009, Sim WJ et al 2010
Antibiotic	Macrolides	Erythromycin	ERY	USA 2, Japan 74.8	Lacey, C. et al., 2008, Mitchell S. et al., 2014 , Narumiya et al., 2009
		Roxithromycin	ROX	EU >1, Japan 35	Robert Loos et al., 2013, Narumiya et al., 2009
	Fluoroquinolones / Quninolones	Levofloxacin	LVF	USA >1, Japan 66	Mitchell S. et al., 2014, Narumiya et al., 2009
		Ciprofloxacin	CIPX	UK 67, USA >1, EU 96.3, Japan 8.84	Lacey, C. et al., 2008, Robert Loos et al., 2013, Mitchell S. et al., 2014, Narumiya et al., 2009,
	Lincosamides	Lincomycin	LVF	UK >1, USA 10, USA(Michigan) 35, Japan 7.35, Korea 1437	Lacey, C. et al., 2008, Mitchell S. et al., 2014, Narumiya et al., 2009, Shishir Kumar Behera et al., 2011
	Sulfonamides	Sulfamethoxazole	SMZ	UK 910, USA 80, USA(Michigan) 178, EU 280, Japan 90.1, Korea 57	Lacey, C. et al., 2008, Robert Loos et al., 2013, Mitchell S. et al., 2014, Narumiya et al., 2009, Sim WJ et al 2010
		Sulfathiazole	STZ	USA >1	Lacey, C. et al., 2008, Mitchell S. et al., 2014, Shishir Kumar Behera et al., 2011
	Cyclines	Oxytetracycline	OXT	USA(Michigan) 17	Lacey, C. et al., 2008
		Tetracycline	TC	USA 10, USA(Michigan) >1, Japan 3.47	Lacey, C. et al., 2008, Narumiya et al., 2009
	Pyrimidines	Trimethoprim	TMP	UK 170, USA 10, EU 229 , Japan 43, Korea 63	Lacey, C. et al., 2008, Robert Loos et al., 2013, Mitchell S. et al., 2014, Narumiya et al., 2009, Sim WJ et al 2010
	Phenols	Triclosan	TRI	USA 10, Korea 112	Lacey, C. et al., 2008, Sim WJ et al 2010
Antiepileptic		Carbamazepine	CMZ	UK 97, USA >1, USA(Michigan) 155, EU 832, Korea 55	Lacey, C. et al., 2008, Robert Loos et al., 2013, Mitchell S. et al., 2014
		Primidone	PRI	USA 46, Japan 46.3, Korea 57	Lacey, C. et al., 2008, Narumiya et al., 2009, Shishir Kumar Behera et al., 2011
Insecticide		DEET	DEET	USA 18, Japan 21.8	Lacey, C. et al., 2008, Mitchell S. et al., 2014 , Narumiya et al., 2009
Antihypertensives		Diltiazem	DTZ	UK 85, EU 10.7, Japan 32.5	Robert Loos et al., 2013, Mitchell S. et al., 2014, Xin Yang et al., 2011, Narumiya et al., 2009
estrogens		Ethynylestradiol	EE2	USA 10	Lacey, C. et al., 2008
Diuretic		Furosemide	FUR	UK 280, Japan 120	Mitchell S. et al., 2014, Narumiya et al., 2009

2.3.4 Comparison of PPCPs in surface waters in the Korea and the other countries

Papers published from 1997 to 2012 say that diverse medical supplies are being developed, antibiotics, non-steroidal anti-inflammatory drugs (NSAIDs), blood lipid lowering agents (BLLAs) and estrogens show a high concentration relatively. Among residual PPCPs detected in each country of the world, we compared 39 kinds relatively high in concentration and occurrence among countries including Korea in terms of maximum concentration and showed them together. Comparisons were made between composition of PPCPs and estrogens in report from many countries and Korea (Figure 2.3), verifying the composition of PPCPs detected. Figure 2.3 is the graph show the maximum concentrations of PPCPs detected from the surface water of each country of the world without considering flow rate. For acetaminophen, UK showed the highest concentration (2,382 ng/L), while for caffeine, Japan showed the highest (7,591 ng/L). For diclofenac, Germany reported the highest detection (15,033 ng/L), for ibuprofen and naproxen, Canada reported the highest (6,400 ng/L and 4,500 ng/L, respectively), and for sulfamethoxazole, Australia reported the highest (2,000 ng/L). Korea showed a higher concentration of acetaminophen, clarithromycin, mefenamic acid, sulfadimethoxine and sulfathiazole, when

compared to other countries. Especially, the concentration of clarithromycin, an antibiotic mainly used for treatment of a number of bacterial infections, was much higher than in Italy.

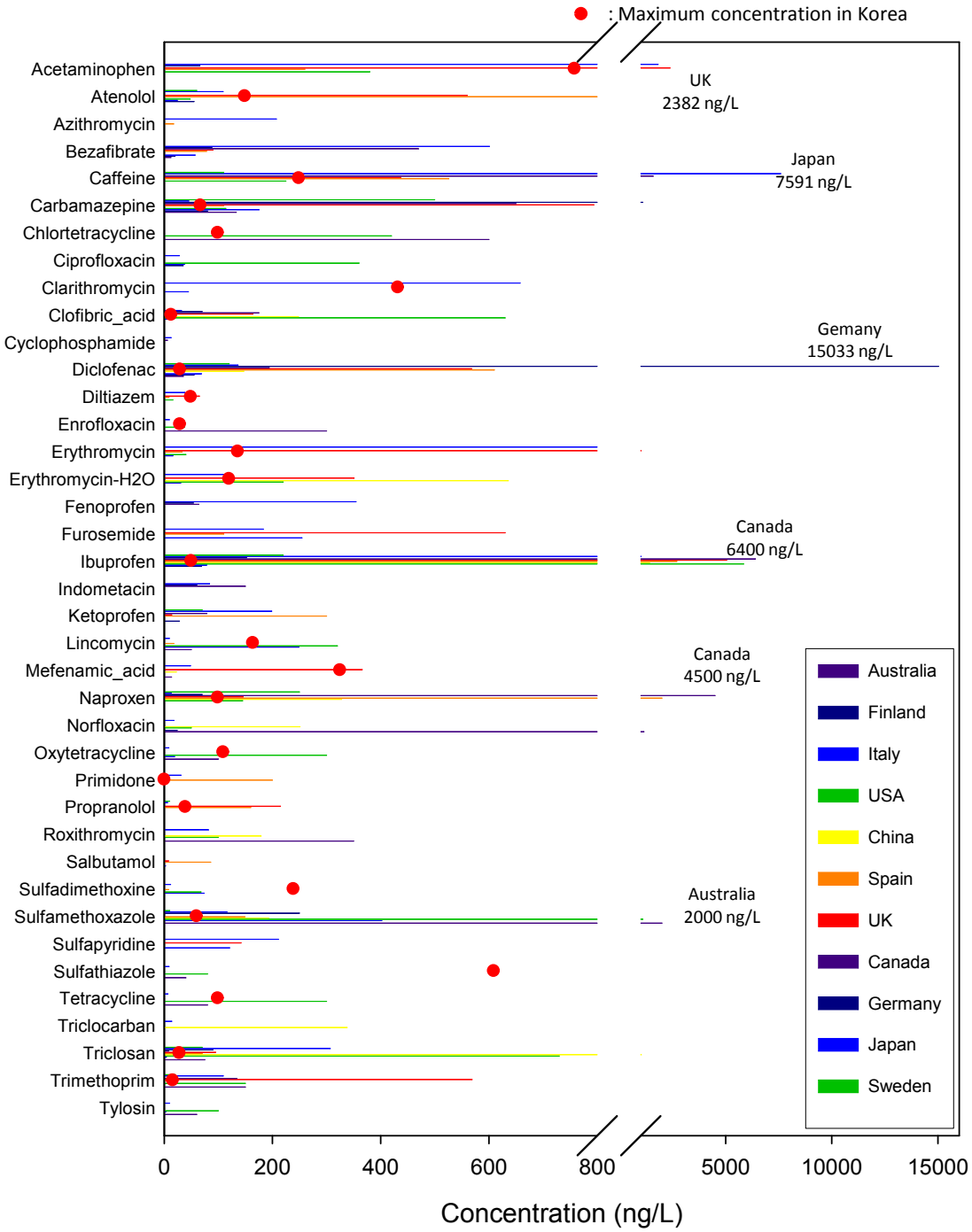


Figure 2.3 Maximum detection concentrations of PPCPs in surface waters in the world

Table 2.5 Summary of pharmaceuticals occurrence in surface waters in the world

No.	Copmpounds	Nation and concentraion (ng/L)	Ref.
1	Acetaminophen	Germany 5-66, UK 1.5-2398, USA N.D.-380, Spain 163-260, Japan max 1819, Korea max 759	Barnes, K. K. et al., 2008; Hilton, M. J. et al., 2003; Reddersen, K. et al., 2003; Stackelberg, P. E. et al., 2007; Kasprzyk-Hordern, B. et al., 2008; Kasprzyk-Hordern, B. et al., 2009; Boleda, M. R. et al., 2011; Conley, J. M. et al., 2008; Grujić, S. et al., 2009; Wiegel, S. et al., 2004, Y. Yoon et al., 2010, Kim, J. W.et al., 2009
2	Atenolol	Finland 11.8-55, Italy 3.44-24.1, Spain max 900, Swedeen 10-60, UK 1-560, USA 10-48, Japan max 108, Korea max **150**	Snyder, S. A. et al., 2008; Calamari, D. et al., 2003; Bendz, D. et al., 2005; Kasprzyk-Hordern, B. et al., 2008; Kasprzyk-Hordern, B. et al., 2008; Zuccato, E. et al., 2005; Vieno, N. M. et al., 2007; Benotti, M. J. et al., 2009, Y. Yoon et al., 2010
3	Azithromycin	Spain 8.0-17.6, Japan max 207	Boleda, M. R. et al., 2011
4	Bezafibrate	Austrlia 1.6-12.5, Finland N.D.-20, Germany 50-88, Italy 0.8-57.2, Spain 26.7-78.4, UK 10-90, Japan max 600	Calamari, D. et al 2003; Kasprzyk-Hordern, B. et al., 2009; Boleda, M. R. et al., 2011; Conley, J. M. et al., 2008; Zuccato, E. et al., 2005; Vieno, N. M. 2007; Wiegel, S. et al., 2004
5	Caffeine	Canada N.D.-1590, Spain 291-526, Sweden 5-110, UK 265-437, USA N.D.-224.8, Japan max 7591, Korea max 250	Bendz, D. et al., 2005; Kasprzyk-Hordern, B. et al., 2008; Kasprzyk-Hordern, B. et al., 2008; Zuccato, E. et al., 2005; Vieno, N. M. et al., 2007; Huerta-Fontela, M. et al., 2008, Y. Yoon et al., 2010
6	Carbamazepine	Austrlia 23.0-133.1, Canada 0.3-650, Finland 1.4-80, Germany 45-1100, India max 128, Italy max 175.3, Spain 2-110, Sweden 1-500, UK 0.5-794, USA N.D.-113.7, Japan max 45, Korea max 68	Hilton, M. J. et al., 2003; Reddersen, K. et al., 2003; Stackelberg, P. E. et al., 2007; Zuccato, E. et al., 2005, Y. Yoon et al., 2010
7	Chlortetracycline	Australia max 600, USA N.D.-420	Stackelberg, P. E. et al., 2007, Watkinson, A. J. et al., 2009
8	Ciprofloxacin	Australia 23-1300, Italy N.D.-37.5, USA N.D.-360, Japan max 28	Zuccato, E. et al., 2005; Watkinson, A. J. et al., 2009
9	Clarithromycin	Italy 0.49-44.76, Japan max 657, Korea max 433	Zuccato, E. et al., 2010, Kim, Y., Jung et al., 2008, Kim, J. W.et al., 2009
10	Clofibric_acid	Canada N.D.-175, Germany 1-70, Italy 0.41-5.77, Spain 10-20, UK 0.3-164, USA N.D.-630, China N.D.-248, Japan max 31, Korea max 14	Kasprzyk-Hordern, B. et al., 2008; Kasprzyk-Hordern, B. et al., 2009; Boleda, M. R. et al., 2011; Conley, J. M. et al., 2008; Grujić, S. et al., 2009; Wiegel, S. et al., 2004; Zhao, J. L. et al., 2010,, Y., Jung et al., 2008
11	Cyclophosphamide	Canada N.D.-6, Italy N.D., Japan max 12	Zuccato, E. et al., 2005; Metcalfe, C. D. et a., 2003;
12	Diclofenac	Austrlia 15.8-35.5, Canada N.D.-194, Finland N.D.-55, Germany N.D.-15033, Spain 2-610, Sweden 10-120, UK 0.5-568, USA max 1.2, China N.D.-147, Japan max 136, Korea max 30	Bendz, D. et al., 2005; Kasprzyk-Hordern, B. et al., 2008; Kasprzyk-Hordern, B. et al., 2008; Zuccato, E. et al., 2005; Vieno, N. M. et al., 2007; Huerta-Fontela, M. et al., 2008, Y. Yoon et al., 2010
13	Diltiazem	Spain 4-9, UK 1-65, USA 1.3-16, Japan max 38, Korea max 50	Zuccato, E. et al., 2005; Metcalfe, C. D. et a., 2003; Huerta-Fontela, M. et al., 2011; Pailler, J. Y. et al., 2004, , Y., Jung et al., 2008
14	Enrofloxacin	Australia max 300, USA N.D.-10, Japan max 9, Korea max 30	Watkinson, A. J. et al., 2009; Kolpin, D. W. et al., 2004, , Y., Jung et al., 2008
15	Erythromycin	Italy 0.8-15.9, Spain 21.4-33.0, UK 10-1022, USA N.D.-40, Japan max 822, Korea max 137	Kagle, J. et al., 2007; Stackelberg, P. E. et al., 2007; Boleda, M. R. et al., 2011; Ashton, D. et al., 2004; Pailler, J. Y. et al., 2004
16	Erythromycin-H2O	Italy 1.7-30.5,UK 0.5-351, USA N.D.-220, China 30-636, Japan max 118, Korea max 121	Zuccato, E. et al., 2010; Kagle, J. et al., 2007; Stackelberg, P. E. et al., 2007; Boleda, M. R. et al., 2011; Ashton, D. et al., 2004
17	Fenoprofen	Canada N.D.-64, Germany 2-54, Japan max 354	Perret, D. et al., 2006; Wiegel, S. et al., 2004; Brun, G. L. et al., 2006; Jux, U. et al., 2002
18	Furosemide	Italy max 254.7, Spain max 110, UK 6-630, Japan max 183	Kasprzyk-Hordern, B. et al., 2008; Kasprzyk-Hordern, B. et al., 2009; Zuccato, E. et al., 2005
19	Ibuprofen	Canada N.D.-6400, Finland N.D.-69, Germany 2-152, Italy N.D.-78.5, Spain 8-2700, Sweden 10-220, UK 0.3-5044, USA N.D.-5850, China N.D.-1417, Japan max 1015, Korea max 51	Calamari, D. et al 2003; Kasprzyk-Hordern, B. et al., 2009; Boleda, M. R. et al., 2011; Conley, J. M. et al., 2008; Zuccato, E. et al., 2005; Vieno, N. M. 2007; Wiegel, S. et al., 2004, Y. Yoon et al., 2010
20	Indometacin	Canada N.D.-150, Germany 5-60, Japan max 83	Metcalfe, C. D. et al., 2003; Wiegel, S. et al., 2004; Brun, G. L. et al., 2006; Jux, U. et al., 2002
21	Ketoprofen	Canada N.D.-79, Finland N.D.-28, Spain N.D.-300, Sweden 10-70, UK 0.5-14, Japan max 198	Kasprzyk-Hordern, B. et al., 2008; Zuccato, E. et al., 2005; Bendz, D. et al., 2005, , Y., Jung et al., 2008
22	Lincomycin	Australia max 50, Italy 3.1-248.9, Spain 13.4-17.9, USA N.D.-320 , Japan max 9.4, Korea max 165	Perret, D. et al., 2006; Wiegel, S. et al., 2004; Brun, G. L. et al., 2006; Jux, U. et al., 2002; Pailler, J. Y. et al., 2004
23	Mefenamic_acid	Austrlia 0.4-13.6, China N.D.-22.4, UK 0.3-366, Japan max 48, Korea max 326	Kagle, J. et al., 2007; Stackelberg, P. E. et al., 2007; Boleda, M. R. et al., 2011; Ashton, D. et al., 2004, , Y., Jung et al., 2008
24	Naproxen	Canada N.D.-4500, Finland N.D.-45, Germany N.D.-70, Spain N.D.-2000, Sweden 90-250, UK 0.3-146, USA N.D.~145, China N.D.-328, Japan max 12, Korea max **100**	Zhao, J. L. et al., 2010; Hilton, M. J. et al., 2003; Reddersen, K. et al., 2003; Stackelberg, P. E. et al., 2007; Kasprzyk-Hordern, B. et al., 2008; Kasprzyk-Hordern, B. et al., 2009, Y. Yoon et al., 2010
25	Norfloxacin	Australia 30-1150, Finland max 24, USA 5-50, China 13-251, Japan max 18	P. E. et al., 2007; Boleda, M. R. et al., 2011; Ashton, D. et al., 2004
26	Oxytetracycline	Australia max 100, Italy N.D.-19.2, USA N.D.-340, Japan max 8, Korea max 11(	Zuccato, E. et al., 2005; Watkinson, A. J. et al., 2009; Zuccato, E. et al., 2010
27	Primidone	Spain mean 39, max 200, Japan max 30, Korea max 1.4	Huerta-Fontela, M. et al., 2008, Y. Yoon et al., 2010
28	Propranolol	Spain max 270, Sweden <1-10, UK 0.5-215, Japan max 6, Korea max 40	Huerta-Fontela, M. et al., 2008; Ashton, D. et al., 2004
29	Roxithromycin	Australia max 350, China 16-179, USA 50-100, Japan max 81	Kagle, J. et al., 2007; Stackelberg, P. E. et al., 2007; Boleda, M. R. et al., 2011; Ashton, D. et al., 2004
30	Salbutamol	Italy max 2.5, Spain max 86, UK <0.5-8, Japan max 0.5	Huerta-Fontela, M. et al., 2008; Stackelberg, P. E. et al., 2007
31	Sulfadimethoxine	Italy 28-74, Spain 8.3, USA N.D.-68, Japan max 11, Korea max 240	Huerta-Fontela, M. et al., 2008; Pailler, J. Y. et al., 2004, Kim, J. W.et al., 2009
32	Sulfamethoxazole	Australia max 2000, China 37-193, Italy N.D.-402, Spain 58-149, Sweden <1-10, USA N.D.-1100, Japan max 115, Korea max 61	Pailler, J. Y. et al., 2004; Boleda, M. R. et al., 2011; Ashton, D. et al., 2004, Y. Yoon et al., 2010
33	Sulfapyridine	Italy <12-121, UK <2-142, Japan max 211	Boleda, M. R. et al., 2011; Ashton, D. et al., 2004
34	Sulfathiazole	Australia max 40, USA N.D.-80, Japan max 9, Korea max 610	Zuccato, E. et al., 2005; Watkinson, A. J. et al., 2009; Pailler, J. Y. et al., 2004
35	Tetracycline	Australia max 80, USA N.D.-300, Japan max 7, Korea max 100	Zuccato, E. et al., 2005; Pailler, J. Y. et al., 2004, Kim, J. W.et al., 2009
36	Triclocarban	China 1.2-338, Japan max 13	Zhao, J. L. et al., 2010
37	Triclosan	Australia <3-75, Canada <4-8, China 1.2-1023, Germany <3-90, India 4-5160, Italy <2.0-4.0, Spain N.D.-285, Sweden N.D.-70, UK <5-95, USA N.D.-730, Japan max 306, Korea max 29	Kasprzyk-Hordern, B. et al., 2008; Kasprzyk-Hordern, B. et al., 2009; Boleda, M. R. et al., 2011; Conley, J. M. et al., 2008; Grujić, S. et al., 2009; Wiegel, S. et al., 2004; Zhao, J. L. et al., 2010, Y. Yoon et al., 2010
38	Trimethoprim	Australia max 150, Canada N.D.-134, Spain 9.5-22.8, Sweden <1-20, UK N.D.-569, USA N.D.-150, Japan max 109, Korea max 17	Kagle, J. et al., 2007; Stackelberg, P. E. et al., 2007; Boleda, M. R. et al., 2011; Ashton, D. et al., 2004; Pailler, J. Y. et al., 2004, Y. Yoon et al., 2010
39	Tylosin	Australia max 60, Italy N.D.-2.77, Spain 0.5-1.6, USA N.D.-100, Japan max 9.8	Zuccato, E. et al., 2005; Watkinson, A. J. et al., 2009

2.4 Veterinary pharmaceuticals (VPs)

2.4.1 Pathway of VPs

The pathway of veterinary pharmaceuticals (VPs) to waterway is different from human pharmaceuticals (Figure 2.4). While human pharmaceuticals discharge into the environment mainly through STPs (Williams, 2005), VPs could enter the environment not only through direct application in aquaculture and wash-off from topical treatments; but also from livestock wastewater treatment plants. The runoff from manure-treated farmlands is also one of the major sources of VPs to the environment. As such, VPs are considered as nonpoint source pollutants, and their environmental concentrations might be affected largely by precipitation (Park et al., 2007). Once released into the environment, pharmaceuticals and their metabolites may run into surface waters or leach to groundwater where they may affect the ecosystem as well as human health.

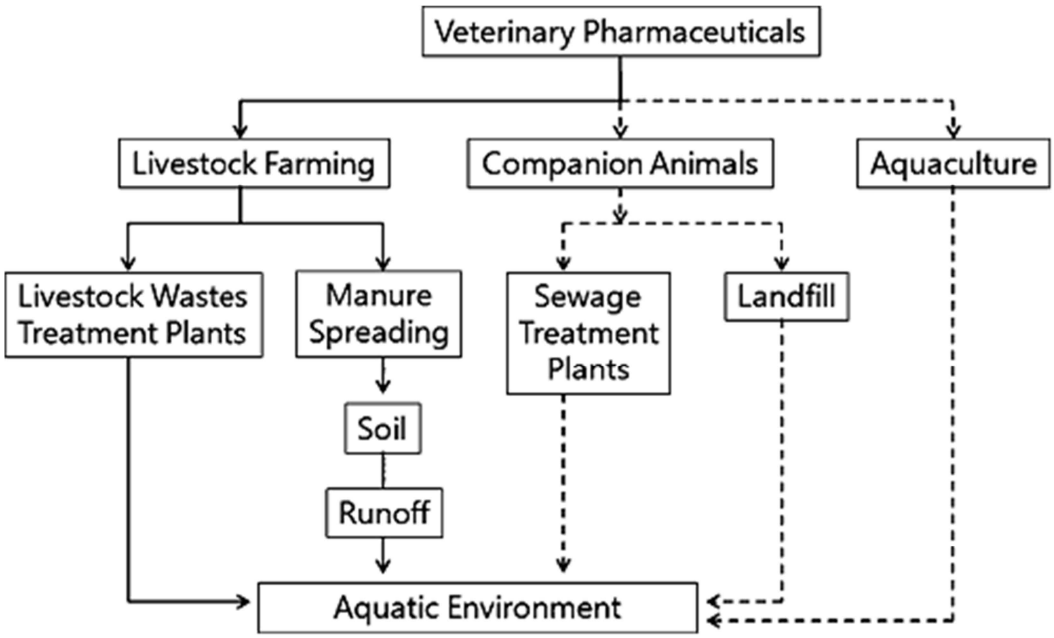


Figure 2.4 Routes of VPs entering the aquatic environment. Bold line indicates major contribution pathways, while dotted line represents relatively minor contribution pathways into the environment.

Though there are many kinds of influent pathway of VPs, VPs mainly detected from the STP, which treats both domestic and livestock wastewater, were verified with research on removal efficiency at the treatment process.

2.4.2 Occurrence of VPs in Korea

Currently, in stockbreeding of Korea, about an annual 1,500ton of antibiotics is recklessly being used not only for treating the livestock disease but also for fostering their growth. Compared to other stockbreeding countries, such as the US, Japan, Denmark, New Zealand and Sweden, Korea

is at a highest level in the antibiotic use against annual livestock output as show in Figure 2.5 (Younghee Kim et al., 2008; Park et al., 2007). Twenty PPCPs were identified in the top priority class in Korea. Among these compounds, 8 were identified as deserving more immediate attention: amoxicillin, enramycin, fenbendazole, florfenicol, ivermectin, oxytetracycline, tylosin, and virginiamycin (Younghee Kim et al., 2008; Park et al., 2007). Denmark produces 1.2 times of livestock output than Korea, while Korea uses 16 times (around 1,000 ton) more antibiotics, Japan produces double livestock output, Korea uses 1.4 times (500 ton) more antibiotics. The US produces livestock output around 24 times than Korea, while the US uses around 3.8 times larger antibiotics than Korea (MFDS. 2006, 2010). Other advanced countries such as New Zealand, Sweden, etc., which have a very strict regulation on stockbreeding and fishery, were turned out to be relatively at very low levels of antibiotic use compared to Korea (MFDS. 2006, 2010). Korean sales (use) of antibiotics for stockbreeding and fishery were 1,538 ton in2005, 1,403 ton in 2007 and 1,593 ton in 2009, respectively (MFDS. 2006, 2010).

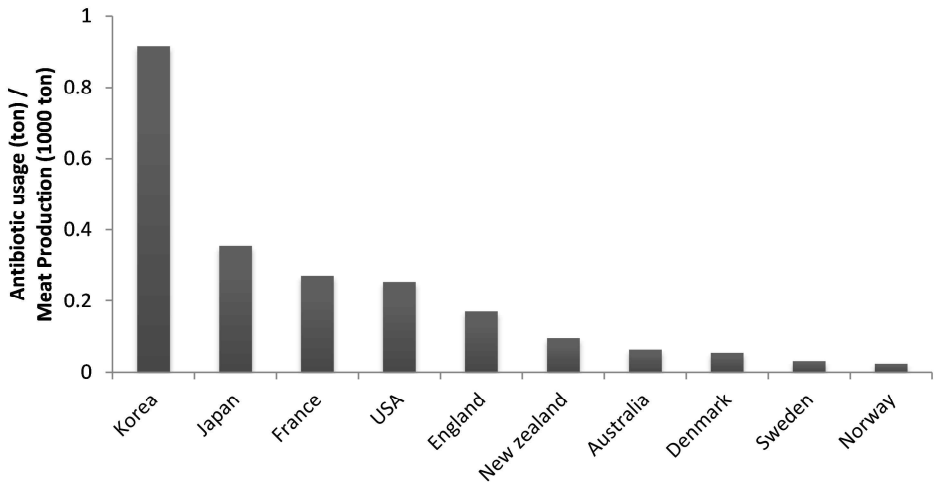


Figure 2.5 Antibiotic usage compared to meat production

2.4.3 Overseas trends

The worldwide variation in the total amounts of VPs used in different countries is shown in Table 2.6. Due to the difficulty in collecting information on the total amount used in individual stock farms, most countries simply devided by the amount sold head or weight of livestock as show in Table 2.6.

Table 2.6 Worldwide variation in the total amount of livestock numbers and VPs used for livestock

Country	Head (×1,000)			Amount used (tonne)				Ref.
	Cattle	Pig	Poultry	Cattle	Pig	Poultry	Total	
Australia	4,500	700	80,700	-	-	-	932	JETACAR et al., 1999
Denmark	1,107	25,785	121,735	11 (9.9)	93 (3.6)	0.4 (0.003)	104.4	DANMAP et al., 2005
Norway	930	802	3,646	-	-	-	6	NORM/NORM-VET et al., 2005
Sweden	-	-	-	-	-	-	16	SAV et al., 2005
UK	10.378	4,851	159,323	7 (0.7)	281 (58)	20 (0.12)	308	VMD et al., 2006
USA	29,000	92,600	780,000	1,675 (58)	4,694 (51)	4,779 (6.1)	11,148	Benbrook et al., 2002
Korea	1,819	8,962	109,628	112 (62)	831 (93)	335 (3.1)	1,278	KFDA 2010

* The values in parenthesis are the amount of veterinary antibiotics used per head (grams head−1)

The USA was the biggest consumer of VPs at 11,148 tons year^{-1} followed by Korea at 1,278 tons year^{-1} (Table 2.6). These usage rates were significantly higher than Australia and many EU countries (Table 2.6), and this was attributed to not only high numbers of livestock in both the USA and Korea but also the common agricultural practice of using VPs as feed supplements for growth promotion in both countries. This was also well evidenced by the calculation of the VPs used per head of livestock in each country (Table 2.6). The EU prohibition on the use of VPs as feed supplements for growth enhancement in 1998 resulted in significant reduction in VPs consumption in European countries. Thus, with the exception of the large amount of VPs used for pig (58 g head^{-1}) in the UK, VPs usage in Europe was generally low. In contrast, no ban on VPs use in the USA has been imposed, and growth promotion antibiotics are still widely used. Comparison of the total amount of VPs used among the three different stock animals indicated that the highest amounts of VPs were used for pig followed by poultry (Table 2.6). This is related to the type of livestock breeding. For effective production, pigs are raised very densely in a limited space, and such animal husbandry practices are likely to be the cause of decreased immunity and higher infection rates among pigs, driving the usage of antibiotic treatments. Among the antibiotic families reviewed, in most countries, tetracyclines were the most commonly used antibiotics followed by sulfonamides and macrolides (Table 2.7).

Table 2.7 Variation of the total amount (tonne) of three antibiotic families used in selected countries

Country	Amount used (tonne)				Ref.
	Total	Tetracycline	Sulfonamides	Macrolides	
Denmark	112	30 (27)	13 (12)	22 (20)	DANMAP et al., 2005
Norway	6	0.3 (5)	1.5 (25)	-	NORM/NORM-VET et al., 2005
Sweden	16.4	1.6 (10)	2.5 (15)	1.0 (6)	SAV et al., 2005
UK	395	240 (61)	74 (19)	37 (9)	VMD et al., 2006
USA	11,148	3,230 (29)	-	-	Benbrook et al., 2002
Korea	1,595	723 (45)	237 (15)	59 (4)	KFDA 2010

For instance, these three antibiotic groups accounted for approximately 90% of the total antibiotics used in the UK, whereas in Korea and Denmark, these three groups accounted for more than 50% of total antibiotic usage. Currently, each country is reducing the use of antibiotics

because its reckless use in stockbreeding and fisheries is considered largely responsible for increasing resistance in the body (Carballa, M. et al., 2004). Sweden, in 1986, banned the use of antibiotics for the purpose of fostering growth, while in 1996 Denmark and Germany banned the use of avoparcin for the reason of resistant bacteria appearing from its use for food animals. Besides, Denmark banned the use of virginiamycin, a streptogramins-descent antibiotic, in 1998. EU, in 1997, banned the use of avoparcin for growth-stimulating purpose and banned again in 1999 the use of carbadox and olaquindox which had been used for artificial additives to feed (Huang C.H. et al., 2001). In Japan, on the other hand, a variety of researches are available. In particular, detailed researches on oxytetracycline, the major VPs substance, are available (A, Seino et al., 2004).

2.4.4 Position of this research

Research papers related to VPs are rarely found in Korea. Despite the strengthening regulations on the use of VPs reported with toxicity and problems as above-mentioned, there are scanty studies on the model for behavior and management in environment. This study identifies quantity and removal characteristics of VPs detected in livestock wastewater in STP, explored VPs problems in Korea and suggested how to manage VPs effectively in Korea. The increasing use of VPs is likely to increase the kinds and quantities of VPs flowing in rivers. This study presented the future direction of research by describing the generation of VPs and treatment efficiency at STP.

2.5 Toxicity

Residual PPCPs and estrogens existing in the water are known to have a harmful influence on aquatic ecosystem. They remain after moving into aquatic environment through diverse sources of discharge, influxes and migratory paths and then seep into living bodies causing a serious influence on the ecosystem and human health. Typical influences include causing reduction in the number of individuals, lowered virility, obstruction to growth and immunity and cancer. For ecological toxicity, aquatic toxicity information was considered first. For the PPCPs and estrogens of which aquatic toxicity information was not available, terrestrial toxicity data were employed. However, for certain compounds, no ecological toxicity information was available because only very limited toxicity information is available for terrestrial toxicity of PPCPs and estrogens. Methods of continually evaluating ecological toxicity quantitatively are in development and the basic approaches include diverse experiments on toxicity using aquatic animals and plants such as water flea, fish and algae. Among the subject creatures, water flea reacts most sensitively to residual PPCPs while algae, fish, etc. are used in high frequency. Appraisal is made on the basis of half effective concentration (EC_{50}), half lethal concentration (LC_{50}), no observed effect concentration (NOEC) and lowest observed effect concentration (LOEC). Table 2.8 shows toxicity classification of the PPCPs and estrogens remaining in aquatic environment while Table 2.9 shows the various results of in vivo toxicity on PPCPs and estrogens remaining in the water (Younghee Kim et al., 2008).

Table 2.8 Toxicity classification of residual PPCPs and estrogens in water environment

Toxicity	LC50, EC50 (fish, crustacean, algae)
Low	> 100 mg/L
Moderate	> 10~100 mg/L
High	1~10 mg/L
Very high	< 1 mg/L

Table 2.9 Determination of hazard classification based on ecological toxicity and human health effect of the PPCPs (Younghee Kim et al., 2008)

Therapeutic use	Compounds	Test organism		Acute toxicity	
		Taxon	Species	Test	Data
Antibiotic					
β-Lactam	Amoxicillin	Algae	M. aeruginosa	EC_{50} (72 h)	0.0037 mg/L, growth inhibition
		Algae	S. capricornutum	NOEC (72 h)	250 mg/L, growth inhibition
		Algae	S. leopoliensis	EC_{50}	2.22 μg/L, growth inhibition
		Algae	S. leopoliensis	NOEC	0.78 μg/L, growth inhibition
		Bacteria	V. fischeri	EC_{50} (15 min)	3597 mg/L, luminescence
	Penicillin G	Algae	M. aeruginosa	EC_{50}	0.006 mg/L, growth rate
		Algae	S. capricornutum	NEOC	100 mg/L, growth rate
Quinolone	Enrofloxacin	Crustacean	D. magna	EC_{50} (48 h)	56.7 mg/L, immobilization
		Crustacean	D. magna	NOEC (21 d)	5 mg/L, reproduction
	Norfloxacin	Algae	S. capricornutum	EC_{50}	16.6 mg/L, growth inhibition
		Algae	S. capricornutum	NEOC	4.01 mg/L, growth inhibition
		Algae	C. vulgaris	EC_{50}	10.4 mg/L, growth inhibition
		Algae	C. vulgaris	NOEC	4.02 mg/L, growth inhibition
		Rotifer	B. calyciflorus	LC_{50} (24 h)	29.88 mg/L, mortality
	Ofloxacin	Algae	M. aeruginosa	EC_{50} (72 h)	0.180 mg/L, growth inhibition
		Algae	P. subcapitata	EC_{50} (72 h)	1.44 mg/L, growth inhibition
		Rotifer	B. calyciflorus	EC_{50} (48 h)	0.53 mg/L, population growth inhibition
		Crustacean	D. magna	EC_{50} (24 h)	31.75 mg/L, immobilization
Lincosamide	Lincomycin	Algae	P. subcapitata	EC_{50} (72 h)	0.07 mg/L, growth inhibition
		Rotifer	B. calyciflorus	LC_{50} (24 h)	24.94 mg/L, mortality
		Rotifer	B. calyciflorus	EC_{50} (48 h)	0.68 mg/L, population growth inhibition
		Crustacean	D. magna	EC_{50} (24 h)	23.18 mg/L, immobilization
		Crustacean	T. platyurus	LC_{50} (24 h)	30.00 mg/L, mortality
Macrolide	Clarithromycin	Algae	P. subcapitata	EC_{50} (72 & 96 h)	72 h: 0.002 mg/L, 96 h: 11 μg/L, growth inhibition
		Algae	P. subcapitata	NOEC (96 h)	3.1 μg/L, growth inhibition
		Crustacean	D. magna	EC_{50} (24 h)	25.72 mg/L, immobilization
		Fish	O. latipes	LC_{50} (96 h)	>100 mg/L, mortality
	Erythromycin	Algae	P. subcapitata	EC_{50} (72 h)	0.02 mg/L, growth inhibition
		Rotifer	B. calyciflorus	LC_{50} (24 h)	27.53 mg/L, mortality
		Rotifer	B. calyciflorus	EC_{50} (48 h)	0.94 mg/L, population growth inhibition
		Crustacean	T. platyurus	LC_{50} (24 h)	17.68 mg/L, mortality
		Crustacean	D. magna	EC_{50} (24 h)	22.45 mg/L, immobilization
		Fish	O. latipes	LC_{50} (96 h)	>100 mg/L, mortality
		Duckweed	Lemna minor	EC_{50} (7 d)	5.62 mg/L, growth inhibition
	Spiramycin	Algae	M. aeruginosa	EC_{50}	0.005 mg/L, growth rate
		Algae	S. capricornutum	EC_{50}	2.3 mg/L, growth rate
	Tylosin	Algae	M. aeruginosa	EC_{50}	0.034 mg/L, growth rate
		Algae	S. capricornutum	EC_{50}	1.38 mg/L, growth rate
		Crustacean	D. magna	EC_{50} (48 h)	680 mg/L, immobilization
		Crustacean	D. magna	NOEC (21 d)	45 mg/L, reproduction
Phenol	Triclosan	Algae	S. subspicatus	NOEC (72 h)	500 ng/L, growth
Pyrimidine	Trimethoprim	Algae	M. aeruginosa	EC_{50} (72 h)	112 mg/L, growth inhibition
		Algae	S. capricornutum	EC_{50} (72 h)	130 mg/L, growth inhibition
		Bacteria	V. fischeri	EC_{50} (15 min)	176.7 mg/L
		Crustacean	D. magna	EC_{50} (48 h)	92 mg/L, immobilization
		Crustacean	M. macrocopa	EC_{50} (48 h)	54.8 mg/L, immobilization
		Cnidarian	Hydra attenuata	LC_{50} (96 h)	>100 mg/L, morphology
		Fish	O. latipes	LC_{50} (48 & 96 h)	>100 mg/L

Table 2.9 (Continued)

Sulfonamide	Sulfadiazine	Algae	M. aeruginosa	EC_{50} (72 h)	0.135 mg/L, growth inhibition
		Algae	S. capricornutum	EC_{50} (72 h)	7.8 mg/L, growth inhibition
		Crustacean	D. magna	EC_{50} (48 h)	212 and 221 mg/L, immobilization
	Sulfadimethoxine	Algae	S. capricornutum	EC_{50} (72 h)	2.3 mg/L, growth inhibition
		Algae	C. vulgaris	EC_{50}	11.2 mg/L, growth inhibition
		Bacteria	V. fischeri	EC_{50} (15 min)	>500 mg/L
		Crustacean	D. magna	EC_{50} (48 & 96 h)	48 h: 248 mg/L, 96 h: 204.5 mg/L, immobilization
		Fish	O. latipes	LC_{50} (48 & 96 h)	>100 mg/L
	Sulfamethazine	Bacteria	V. fischeri	EC_{50} (15 min)	344.7 mg/L
		Crustacean	D. magna	EC_{50} (48 & 96 h)	48 h: 174.4 mg/L, 96 h: 158.8 mg/L, immobilization
		Fish	O. latipes	LC_{50} (48 h)	>100 mg/L
	Sulfamethoxazole	Algae	P. subcapitata	EC_{50} (72 h)	0.52 mg/L, growth inhibition
		Algae	S. capricornutum	EC_{50}	1.53 mg/L, growth inhibition
		Bacteria	V. fischeri	EC_{50} (15 & 30 min)	15 min: 78.1 mg/L, 30 min: 23.3 mg/L, luminescence
		Crustacean	D. magna	EC_{50} (24 h)	25.2 mg/L, immobilization
		Cnidarian	Hydra attenuata	LC_{50} (96 h)	>100 mg/L, morphology
		Rotifer	B. calyciflorus	LC_{50} (24 h)	26.27 mg/L, mortality
		Rotifer	B. calyciflorus	EC_{50} (48 h)	9.63 mg/L, population growth inhibition
		Fish	O. latipes	LC_{50} (48 h)	>750 mg/L
	Sulfapyridine	Cnidarian	H. attenuata	LC_{50} & EC_{50} (96 h)	LC_{50}: >100 mg/L, EC_{50}: 21. 61 mg/L, morphology
	Sulfathiazole	Bacteria	V. fischeri	EC_{50} (15 & 30 min)	>1000 mg/L
		Crustacean	D. magna	EC_{50} (48 & 96 h)	48 h: 149.3 mg/L, 96 h: 85.4 mg/L, immobilization
		Fish	O. latipes	LC_{50} (48 & 96 h)	>500 mg/L
Tetracycline	Chlortetracycline	Algae	M. aeruginosa	EC_{50}	0.05 mg/L, growth inhibition
		Bacteria	V. fischeri	EC_{50} (15 min)	13.0 mg/L, luminescence
		Crustacean	D. magna	EC_{50} (24 & 48 h)	24 h: 380.1 mg/L, 48 h: 225 mg/L, immobilization
		Fish	O. latipes	LC_{50} (24 & 48 h)	24 h: 88.4 mg/L, 48 h: 78.9 mg/L, mortality
	Oxytetracycline	Algae	M. aeruginosa	EC_{50} (72 h)	0.207 mg/L, growth inhibition
		Bacteria	V. fischeri	EC_{50} (15 & 30 min)	15 min: 87 mg/L, 30 min: 64.5 mg/L, luminescence
		Rotifer	B. calyciflorus	LC_{50} (24 h)	34.21 mg/L, mortality
		Cnidarian	H. attenuata	LC_{50} & EC_{50} (96 h)	LC_{50}: >100 mg/L, EC_{50}: 40.13 mg/L, morphology
		Crustacean	C. dubia	EC_{50} (24 h & 7 d)	24 h: 18.65 mg/L, immobilization, 7 d: 0.18 mg/L, population growth inhibition
		Fish	O. latipes	LC_{50} (24 & 48 h)	24 h: 215.4 mg/L, 48 h: 110.1 mg/L, mortality
	Tetracycline	Algae	M. aeruginosa	EC_{50}	0.09 mg/L, growth rate
		Algae	S. capricornutum	EC_{50}	2.2 mg/L, growth rate
		Crustacean	D. magna	EC_{50} (21 d)	44.8 mg/L, reproduction
		Duckweed	L. minor	EC_{50} (7 d)	1.06 mg/L, growth inhibition
Others	Metronidazole	Crustacean	D. magna	NOEC (21 d)	250 mg/L, reproduction
Antidepressant	Citalopram	Crustacean	C. dubia	LC_{50} (48 h)	3.9 mg/L,
	Diazepam	Algae	T. chuii	IC_{50}	16.5 mg/L
		Crustacean			12.2 mg/L
		Crustacean	D. magna	LC_{50}	13.9 mg/L
		Cnidarian	H. vulgaris	capacity of regenerate polyps	<1 mg/L, chronic toxicity: 10 µg/L
	Fluoxetine	Algae	D. tertiolecta	EC_{50} (96 h)	169.81 µg/L, growth inhibition
		Algae	P. subcapitata	EC_{50} (120 h)	24 µg/L, growth
		Crustacean	C. dubia	LC_{50} (48 h)	234 µg/L
		Crustacean	D. magna	LC_{50} (48 h)	820 µg/L
		Fish	P. pimelas	LC_{50} (48 h)	705 µg/L
	Paroxetine	Crustacean	C. dubia	LC_{50} (48 h)	0.58 mg/L,

Table 2.9 (Continued)

	Sertraline	Algae	P. subcapitata	EC_{50} & NOEC (72 h)	0.14 & 0.05 mg/L, inhibition
		Algae	P. subcapitata	IC_{50} (96 h)	98.92 µg/L, growth inhibition
		Crustacean	D. magna	EC_{50} & NOEC (48 h)	1.3 & 0.1 mg/L, immobilization
		Crustacean	D. magna	EC_{50} & NOEC (21 d)	0.066 & 0.032 mg/L, reproduction
		Shrimp	T. platyurus	LC_{50} & NOEC (24 h)	0.6 & 0.4 mg/L, lethality
		Fish	O. mykiss	LC_{50} & NOEC (96 h)	0.38 & 0.1 mg/L, lethality
Antiepileptic	Carbamazepine	Algae	D. subspicatus	EC_{50}	74 mg/L, growth inhibition
		Algae	P. subcapitata	NOEC (96 h)	100,000 µg/L, growth inhibition
		Bacteria	V. fischeri	EC_{50} (15 & 30 min)	15 min: 52.2 mg/L, 30 min: >81,000 µg/L
		Crustacean	D. magna	EC_{50} (48 h)	>100 mg/L & >13,800 µg/L, immobilization
		Cnidarian	Hydra attenuata	LC_{50} & EC_{50} (96 h)	LC_{50}: 29.4 mg/L, EC_{50}: 15.52 mg/L, morphology
		Fish	O. latipes	LC_{50} (48 & 96 h)	48 h: 35.4 mg/L, 96 h: 35.4 & 45.87 mg/L, mortality
		Duckweed	L. minor	EC_{50} (7 d)	25.5 mg/L, growth inhibition
Antineoplastic	Cyclophosphamide	Algae	P. subcapitata	EC_{50} & NOEC (72 h)	>100 mg/L, growth inhibition
		Crustacean	D. magna	EC_{50} (21 d)	>100 mg/L, reproduction
	Tamoxifen	Rotifer	B. calyciflorus	LC_{50} (24 h)	0.97 mg/L, mortality
		Crustacean	D. magna	EC_{50} (24 h)	1.53 mg/L, immobilization
		Crustacean	T. platyurus	LC_{50} (24 h)	0.40 mg/L, mortality
Beta-blocker	Atenolol	Algae	D. subspicatus	EC_{50}	620 mg/L, growth inhibition
		Crustacean	D. magna	EC_{50} (48 h)	313 mg/L, immobilization
		Fish	O. latipes	LC_{50} (96 h)	>100 mg/L, mortality
	Metoprolol	Algae	D. subspicatus	EC_{50}	7.3 mg/L, growth inhibition
		Crustacean	D. magna	EC_{50} (48 h)	>100 & 438 mg/L, immobilization
		Fish	O. latipes	LC_{50} (48 h)	>100 mg/L, mortality
	Propranolol	Algae	D. subspicatus	EC_{50} & EC_{50} (48 h)	5.8 & 0.7 mg/L, growth inhibition
		Crustacean	D. magna	EC_{50} (48 h)	7.5 & 7.7 mg/L, immobilization
		Fish	O. latipes	LC_{50} (48 & 96 h)	48 h: 24.3 mg/L, 96 h: 11.4 mg/L, mortality
		Duckweed	L. minor	EC_{50} & EC_{50} (7 d)	113 & 114 mg/L, growth rate and growth inhibition
BLLA					
Fibrate	Bezafibrate	Rotifer	B. calyciflorus	LC_{50} (24 h)	60.91 mg/L, mortality
		Crustacean	D. magna	EC_{50} (24 h)	100.08 mg/L, immobilization
		Cnidarian	H. attenuata	LC_{50} & EC_{50} (96 h)	LC_{50}: 70.71 mg/L, EC_{50}: 25.85 mg/L, morphology
	Clofibrate	Fish	D. rerio	LC_{50} (96 h)	0.89 mg/L, mortality
	Clofibric acid*	Algae	D. subspicatus	EC_{50}	115 mg/L, growth inhibition
		Bacteria	V. fischeri	EC_{50} (30 min)	100 mg/L
		Ciliates	T. pyriformis	EC_{50} (48 h)	175 mg/L, growth inhibition
		Crustacean	D. magna	EC_{50} (48 h)	72 mg/L & >200 mg/L, immobilization
		Duckweed	L. minor	EC_{50} (7 d)	12.5 mg/L, growth inhibition
	Gemfibrozil	Algae	C. vulgaris	EC_{50} (24 h)	195 mg/L, growth
		Algae	P. subcapitata	EC_{50} (72 h)	15.19 mg/L, growth inhibition
		Bacteria	V. fischeri	EC_{50} (0.5, 24 & 48 h)	85.74, 64.6 & 45.1 mg/L, bioluminescence
		Crustacean	D. magna	EC_{50} (24, 48 & 72 h)	57.1, 42.6 & 30.0 mg/L, immobilization
Statin	Atorvastatin	Duckweed	L. gibba	LOEC (7 d)	300 µg/L, growth parameters
	Simvastatin	Algae	D. tertiolecta	EC_{50} (96 h)	22.8 mg/L, growth inhibition
		Copepod	N. spinipes	LC_{50} (96 h) & LOEC	LC_{50}: 810 µg/L & LOEC: 0.16 µg/L, growth rate
		Grass shrimp	P. pugio	LC_{50} (96 h) & NOEC	1.18 & 0.625 mg/L, larvae survival
Contrast media	Iopromide	Algae	S. subspicatus	EC_{50} (72 h)	>10.0 g/L, growth inhibition
		Bacteria	V. fischeri	EC_{50} (30 min)	>10.0 g/L, luminescence
		Crustacean	D. magna	EC_{50} (24 & 48 h)	>10.0 & >1 g/L, immobilization
		Fish	L. idus	LC_{50} (48 h)	>10.0 g/L, mortality

Table 2.9 (Continued)

NSAID	Diclofenac	Algae	D. subspicatus	EC_{50}	71.9 & 72 mg/L, growth inhibition
		Algae	P. subcapitata	NOEC & LOEC (96 h)	10,000 & 20,000 μg/L, growth inhibition
		Bacteria	V. fischeri	EC_{50} (30 min)	11,454 v
		Crustacean	D. magna	EC_{50} (48 h)	22.43 & 68 mg/L, immobilization
		Fish	O. mykiss	LOEC (28 d)	1 & 5 μg/L, histopathological & cytological alterations
		Fish	D. rerio	NOEC & LOEC (10 d)	4000 & 8000 μg/L, survival
		Duckweed	L. minor	EC_{50} (7 d)	7.5 mg/L, growth inhibition
	Ibuprofen	Algae	D. subspicatus	EC_{50}	315 & 342.2 mg/L, growth inhibition
		Crustacean	D. magna	EC_{50} (48 h)	1~100, 101.2 & 108 mg/L, immobilization
		Crustacean	T. platyurus	LC_{50} (24 h)	19.59 mg/L, mortality
		Cnidarian	H. attenuata	LC_{50} & EC_{50} (96 h)	LC_{50}: 22.36 mg/L & EC_{50}: 1.65 mg/L, morphology
		Mollusc	P. carinatus	LC_{50} (72 h)	17.1 mg/L, survival
		Mollusc	P. carinatus	NOEC (21 d)	5.36 mg/L: survival, 1.02 mg/L: growth
		Fish	O. latipes	LC_{50} (96 h)	>100 mg/L, mortality
	Indomethacin	Crustacean	T. platyurus	LC_{50} (24 h)	16.14 mg/L, mortality
		Fish	O. latipes	LC_{50} (96 h)	81.92 mg/L, mortality
	Mefenamic acid	Crustacean	T. platyurus	LC_{50} (24 h)	3.95 mg/L, mortality
		Fish	O. latipes	LC_{50} (96 h)	8.04 mg/L, mortality
	Naproxen	Algae	D. subspicatus	EC_{50}	>320 & 625.5 mg/L, growth inhibition
		Algae	P. subcapitata	EC_{50} (72 h)	31.82 mg/L, growth inhibition
		Rotifer	B. calyciflorus	EC_{50} (48 h)	0.56 mg/L, growth inhibition
		Rotifer	T. platyurus	LC_{50} (24 h)	84.09 mg/L
		Crustacean	D. magna	EC_{50} (48 h)	166.3 & 174 mg/L, immobilization
		Crustacean	C. dubia	EC_{50} (24 h)	66.37 mg/L, immobilization
		Cnidarian	H. attenuata	LC_{50} & EC_{50} (96 h)	LC_{50}: 22.36 mg/L & EC_{50}: 2.62 mg/L, morphology
		Duckweed	L. minor	EC_{50} (7 d)	24.2 mg/L, growth inhibition
	Salicylic acid	Algae	S. subspicatus	EC_{50} (72 h)	>100 mg/L
		Bacteria	V. fischeri	EC_{50} (30 min)	90 mg/L
		Ciliates	T. pyriformis	EC_{50} (48 h)	>100 mg/L, growth inhibition
		Crustacean	D. magna	EC_{50} (24 h)	118 mg/L, immobilization
Estrogens	17β-Estradiol	Fish	O. latipes	NOEC & LOEC (21 d)	<29.3 & 26.3 ng/L, testis-ova induction
	17α-Ethinylestradiol	Fish	P. promelas	LOEC (21 d)	1 ng/L, plasma VTG induction & ultrastructure testes

EC_{50}: half effective concentration, LC_{50}: half lethal concentration, IC_{50}: half inhibitory concentration, NOEC: no observed effect concentration, LOEC: lowest observed effect concentration

The toxicity data of PPCPs, especially aquatic toxicity is not extensively studied and the previous study also pointed out their lack of information for risk assessment carried out human risk assessment of PPCPs by showing relative completeness data of human toxicity instead of using severity of toxicity. However, this lack of toxicity data for the strength of the prioritization still remains as the further step to be taken (KFDA. 2006; KAHPA. 2001; KAHPA. 2005). Diverse studies should proceed as to the toxic influences of various PPCPs and estrogens coexisting in the water on aquatic life rather than such influences of individual chemicals.

2.5.1 Ecological toxicity of PPCPs and estrogens

There is an increasing body of reports on the toxicity of PPCPs and estrogens. Such Known toxicity is also increasing attention to these substances. First, NSAIDs include diclofenac, ibuprofen, naproxen and acetaminophen, which are widely known for high frequencies of detection in STP effluents and rivers. According to reports, these substances show toxicity in phytoplankton and fishes in the river and, especially, acetaminophen may induce toxicity in low concentrations (Santos, L. H. M. L. M. et al., 2010)

As to antibiotics, there is a great variety of substances grouped into many including β-lactam, cycline, lincosamide, macrolide, sulfonamide, quinolone and pyrimidine descents. Besides, since these are prescribed in higher concentrations on man or animal, compared to other medical substances, it is highly probable that large quantities of antibiotics may be introduced to environment (Santos, L. H. M. L. M. et al., 2010). Thus, what matters most is how to cope with the appearance of bacteria resistant to antibiotics caused by their continued exposure to environment and its resultant decrease in the effect of treatment with antibiotics.

BLLAs are chiefly prescribed to lower the concentration of blood cholesterol (Santos, L. H. M. L. M. et al., 2010). These are sorted into stain and fibrate, the latter of which is reported to be chiefly detected in environment (Mimeault, C. et al., 2005). Reports also say that fibrate-gemfibrozil can induce endocrine system orders, while clofibric acid, a metabolite of clofibrate, is often detected in STP effluent and river water due to its characteristic of uneasy decomposition. Estrogen is a female hormone most frequently detected from environment while ethinylestradiol (EE2), typically used for oral contraceptive pill, is known to cause strong endocrine disorders to underwater fishes (Crane, M. et al., 2006). Estrogen detected from environment is bio-accumulated in aquatic life with such reported problems as sexual disturbance, sterility, etc.

2.5.2 Position of this research

This doctoral dissertation was based on study of 61 kinds of PPCPs and estrogen. We can get lots of information with a single analysis because this simultaneously analyzes diverse PPCPs often reported of detection from environment. This research covers more PPCPs variety than other researches that have been done so far and therefore more information can be obtained as a result. Also, the research covers not only PPCPs used by human but also used to animals, which enables us to obtain more accurate interpretation at STPs and in the rivers. Also, by analyzing PPCPs and estrogens remaining in sludge, possibility of discharging them to the environment and their removal in the STPs can be more readily identified. With the prospect of continued increase in the use of PPCPs, load of sewage treatment facilities will keep increasing, too. Thus, to secure the safety of sources, this study presents the research direction for physicochemical behavior and management of PPCPs and estrogens in water environment.

2.6 Modeling of predicted PPCPs and estrogens in the water environment

2.6.1 Seasonal variability of concentrations of PPCPs and estrogens

Relatively few studies have considered the seasonal variability of PPCPs and estrogens concentrations in the environment (Brun GL. et al., 2006). Nonetheless, these studies suggest that PPCPs and estrogens concentrations are influenced by several seasonally varying factors, including chemical consumption, rainfall events, flow rate, and temperature. Seasonal factors influencing human use of specific PPCPs include elevated consumption of ibuprofen and naproxen during the cold and flu season, and increased usage of DEET during the summer months (Kormos JL et al., 2007). In contrast to these over-the-counter remedies, gemfibrozil and carbamazepine are prescribed pharmaceuticals for treatment of chronic conditions and are therefore consumed at a relatively constant rate throughout the year (Conkle JL. et al., 2008; Kormos JL et al., 2007). High discharge rates associated with spring melt and seasonal rainfall events may reduce the efficiency of STPs, resulting in elevated PPCPs and estrogens loadings in surface water (T Tixier C. et al., 2003; Vieno NM. et al., 2007a). In contrast, summer time exposure of PPCPs and estrogens to long periods of sunlight may increase the removal efficiency of some types of treatment (Brun GL. et al., 2006). Although there is some disagreement in the literature, there is evidence that the removal efficiency of STP is highly dependent upon temperature and is likely to be lowest during the winter. Furthermore, in surface waters and other natural systems, temperature can significantly influence biodegradation, photolysis and sorption (Brun GL. et al., 2006). For some compounds, such as ibuprofen and naproxen, the different processes are influenced in opposing ways such that the overall degradation behavior does not vary significantly across seasons.

2.6.2 Modeling of predicted environmental concentrations

The modeling the transport of PPCPs as well as predicting their concentrations in surface waters is critical to understand the potential impact of these compounds on the environment. For example, the PhATE (Pharmaceutical Assessment and Transport Evaluation) model was developed by the Pharmaceutical Research and Manufactures of America (PhRMA) to simulate concentrations of active pharmaceutical ingredients in eleven watersheds across the United States (Anderson PD. et al., 2004). Similarly, the GREAT-ER (Geography-Referenced Regional Exposure Assessment Tool for European Rivers) model was developed as a means of predicting the concentrations of aquatic chemicals as well as the distribution of the concentrations of these compounds in European surface waters (Feijtel T. et al., 1997). These models can be used to estimate the potential risk of aquatic chemicals in the environment at both national and regional scales. Furthermore, the models allow an assessment of the relative influence of different biotic and abiotic processes on the elimination of PPCPs and estrogenic compounds in surface waters. These models can help guide the design of a cost-effective field sampling strategy by highlighting the stream segments with higher potential risk. The PhATE model is also summarized in Table 2.10 along with the GREAT-ER model. As indicated in Table 2.6, there are many similarities between the two models and study results are likely applicable to both models (Hannah R. et al., 2009). So there are diverse studies reported on evaluating the concentrations of PPCPs or estrogens by using or revising these two models.

Table 2.10 Comparison of the Features and Capabilities of the PhATE and GREAT-ER models

	PhATE	GREAT-ER
Watersheds applied	On 11 Watersheds in the US	On 16 European Watersheds
Assumptions	Uses steady-state deterministic mass balance equations	
Segmentation	Only the rivers that receive mass of the chemical compounds from upstream or STPs are considered in the model and segmented with relatively constant characteristics	All rivers in the watershed are considered in the model and segmented with relatively constant characteristics
Mixing in the system	Rivers are considered as plug flow, and lake and reservoirs are considered as completely mixed tanks	
Basic Input Parameters	Usage per capita, in-stream first-order loss, human loss, removal efficiency for each STP treatment type loss.	
Parameters Distribution	Not directly supported	Distribution of the parameters can be specified by the user
Hydrological Regime	Deterministic (mean flow and low flow)	Stochastic (Monte-Carlo to generate variation in flow and velocity)
Data Storage	MS Access, GIS	GIS and DBF
Adding New Watershed	Requires several changes in MS Access	Requires full GIS functionality including ARC/INFO

2.6.3 Position of this research

Ambiguity in the chemical and physical properties of PPCPs and estrogens as well as uncertainty in the hydrological characteristics of a given watershed can significantly reduce the predictive capabilities of the PhATE and GREAT-ER models. Similarly, various parameter assumptions (photolysis, biodegradation and adsorption) can further increase model predictive capabilities. Thus, this study experimented on the factors needed in the target area and then used them for estimation. We presented future direction of research by making factors produced in the target area possible for more accurate estimation than the existing models.

2.7 Conclusions

In Chapter II, studies on PPCPs and estrogens reported so far and its predictive models were examined. The findings from this literature review were as follows;

1) There are not many studies on PPCPs and estrogens in aquatic environment available in Korea. There are only a few studies on kinds and behavior of PPCPs mainly being used in

Korea and even the existing studies are based on the results of researches done in the past.

2) There are virtually no researches available on occurrence of VPs and their behaviors at STP and in the rivers. Study is needed on how PPCPs and estrogens are treated at STP and whether the existing process is suitable or not.

3) Recently, there have been reports on toxic nature of VPs and therefore researches on VPs that occur in Korea are needed.

4) Though models used in the past were able to predict the concentrations of chemicals at rivers, they didn't consider elements of reducing in the river. Studies on models appropriate for STP and rivers of Korea are in need. What we need is to build a model capable of exact prediction of target compounds in the river and effective basin management. If more upgraded model can be developed, it may be possible to suggest a method to manage micropollutants such as PPCPs and estrogens to protect river basins.

5) Centering on PPCPs and estrogens that can make harmful effect on ecosystem and humans, this is an important study that describes their inflow, outflow, kinds, behavior, estimation, present situation of contamination and control to present the direction and content of future research.

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CHAPTER III

OCCURRENCE OF PPCPS AND ESTROGENS IN KOREAN SEWAGE TREATMENT PLANTS IN COMPARISON WITH VARIOUS TYPES OF TREATMENT PROCESSES

3.1 Introduction

Various reports have been published on pharmaceuticals and personal care products (PPCPs) and estrogens in the last few decades (Basile et al., 2011; Boxall et al., 2012; Yong Yu et al., 2013; Kim ilho et al., 2009). PPCPs are widely used for the purpose of treating and preventing human disease. They are also used in farming, livestock, and fishing industries for treating and preventing disease, promoting growth of animals and plants, improving immunity, etc (Boxall et al., 2002; Halling-Sørensen et al., 2002). Various types of PPCPs are produced and prescribed globally, and their variety and production quantities are increasing (Halling-Sørensen et al., 1998; Glassmeyer et al., 2009; Kim Y. et al., 2008). PPCPs are designed to be stable and resist biodegradation inside human body until the pharmacological action is performed; thus, PPCPs are not completely metabolized in the body and are discharged via urine and feces (Fent et al., 2006). Potential pathways of PPCPs and estrogens into the environment include: discharge from factories, effluent from sewage treatment plants (STPs), direct inflow from aquatic fish farms and treatment of agricultural land with manure (Sheyla et al., 2013). Among these routes, STP effluents are one of the most noteworthy sources of PPCPs and estrogens contamination in the environment (Sandeep and Andrew, 2013). PPCPs and estrogens that flow into STPs are treated with various biological treatments and disinfections. Untreated PPCPs and estrogens that flow into rivers result in bioaccumulation and toxicity (Fent et al., 2006; Halling-Sørensen et al., 1998). Such PPCPs exist in extremely low concentrations in the aquatic environment, yet constantly exert a toxic influence on the aquatic environment (Halling-Sørensen et al., 1998; Dorne et al., 2007; Hao et al., 2007; Yamamoto et al., 2007). As the reports on the toxicity of PPCPs and estrogens are increasing, the interest on this issue is also growing and many studies on PPCPs and estrogens in STPs have also been reported (Mojca et al., 2013; Sergio et al., 2013; Sandeep and Andrew, 2013). So, STPs play an important role in managing and controlling the flow of PPCPs and estrogens into the aquatic environment. It is necessary to investigate the substances and their concentrations that flow into STPs in Korea to understand which treatment processes in the STPs are appropriate for removing PPCPs and estrogens. So to control PPCPs and estrogens in the river effectively, it is absolutely needed to study on the characteristics and removal efficiency of PPCPs and estrogens detected from STPs.

In this chapter, Concentrations and characteristics of PPCPs and estrogens detected from influent and effluent of six STPs located at the study area were studied. The characteristics of PPCPs and

estrogens detected in Korean STPs and the removal efficiencies by different biological treatment and chemical treatment of various disinfections were compared. Then PPCPs and estrogens detected from the influent by season were compared to study the kinds of PPCPs chiefly used. In this way, contamination levels of PPCPs and estrogens remaining in the influent and effluent of Korean STPs were verified. Furthermore, this chapter aims at suggesting appropriate biological treatments and chemical treatments for STPs for effective management of PPCPs and estrogens. Lastly, results of this chapter use the occurrence of PPCPs and estrogens and removal efficiency by treating process in building the models of Chapter VI and VII.

3.2 Materials and methods

3.2.1 Chemicals and standards

We analyses 61 PPCPs, three natural estrogens [estrone (E1), 17β-estradiol (E2), and estriol (E3)], one synthesis estrogen [17α-ethynylestradiol (EE2)] in all samples. Separate stock solutions of each standard were prepared at 10 mg L^{-1} by dissolving the appropriate amount of standards in methanol (MeOH) and kept at -20 °C temperature. In this study, classify the compounds into non-steroidal anti-inflammatory drugs (NSAIDs), antibiotics, blood lipid lowering agents (BLLAs), estrogens and many others things (Table 3.1 and Table 3.2).

Table 3.1 Target compounds in this study

Therapeutic use		Compounds (parent compounds and metabolites)
NSAIDs (non-steroidal anti-inflammatory drugs)		Paracetamol (Acetaminophen), Antipyrine, Diclofenac, Ethenzamide, Fenoprofen, Ibuprofen, Indometacin, Ketoprofen, Mefenamic acid, Naproxen, Sulfapyridine
Antibiotic: Cyclines, Fluoroquinolones / Quninolones, Lincosamides, Macrolides, Phenols, Pyrimidines, Sulfonamides, Other chemical classes		Azithromycin, Ceftiofur, Chlortetracycline, Ciprofloxacin, Clarithromycin, Enrofloxacin, Erythromycin, Erythromycin-H2O, Levofloxacin, Lincomycin, Nalidixic acid, Norfloxacin, Oxytetracycline, Roxithromycin, Sulfadimethoxine, Sulfadimidine, Sulfamerazine, Sulfamethoxazole, Sulfamonomethoxine, Sulfathiazole, Tetracycline, Triclocarban, Triclosan, Trimethoprim, Tylosin
BLLAs (blood lipid lowering agents)		Bezafibrate, Clofibric acid
Estrogens		Estrone (E1), 17β-estradiol (E2), estriol (E3), 17α-ethynylestradiol (EE2)
Others	Anticonvulsant	Carbamazepine, Primidone
	Antianginal	Ifenprodil
	Antiarrhythmic	Disopyramide
	Antifungal	Griseofulvin
	Antihypertensive	Diltiazem
	Beta blocker	Atenolol, Metoprolol, Propanolol
	Bronchodilator	Clenbuterol, Salbutamol
	Diuretic	Furosemide
	Psycho-stimulant	Caffeine
	Others	2QCA[*1], Crotamiton, DEET[*2], Dipyridamole, Isopropylantipyrine, Pirenzepine, Sulpiride, Theophylline, Thiamphenicol, Tiamulin

※1 2QCA : 2-quinoxaline carboxylic acid, ※2 DEET : N, N-Diethyl-m-tolamide

Table 3.2 Physicochemical properties of PPCPs

Compounds	CAS	Abbreviation	Mol. wt.	Molecular formula	Water solubility (mg/L, 25°C)	pKa	Log Kow
2-quinoxaline carboxylic acid	879-65-2	2QCA	174.15	C9 H6 N2 O2	—	2.8	—
Acetaminophen	103-90-2	ACT	151.17	C8 H9 N O2	1.4E+04	9.4	0.46
Antipyrine	60-80-0	ANP	188.23	C11 H12 N2 O	5.2E+04	1.4	0.38
Atenolol	29122-68-7	ATL	266.34	C14 H22 N2 O3	1.3E+04	9.6	0.16
Azithromycin	83905-01-5	AZI	749.00	C38 H72 N2 O12	7.1E+00	8.7	4.0
Bezafibrate	41859-67-0	BZF	361.83	C19 H20 Cl N O4	3.4E-01	3.4	4.3
Caffeine	58-08-2	CAF	194.19	C8 H10 N4 O2	2.2E+04	0.8	-0.07
Carbamazepine	298-46-4	CMZ	236.27	C15 H12 N2 O	1.8E+01	13.9	2.5
Chlortetracycline	57-62-5	CTC	478.89	C22 H23 Cl N2 O8	6.3E+02	3.3, 7.7, 9.7	—
Ciprofloxacin	93107-08-5	CIPX	367.81	C17 H18 F N3 O3	3.0E+04	6.2, 8.6	—
Clarithromycin	081103-11-9	CLA	747.97	C38 H69 N O13	3.4E-01	9	3.2
Clenbuterol	37148-27-9	CLB	277.20	C12 H18 Cl2 N2 O	3.3E+03	9.3	2.0
Clofibric acid	882-09-7	CFA	214.65	C10 H11 Cl O3	5.8E+02	3.6	2.6
Crotamiton	483-63-6	CRT	203.28	C13 H17 N O	5.5E+02	—	2.7
Diclofenac	15307-79-6	DCF	319.14	C14 H11 Cl2 N O2	2.4E+00	4.2	0.70
DEET	134-62-3	DEET	191.27	C12 H17 N O	9.1E+02	—	2.2
Diltiazem	33286-22-5	DTZ	450.99	C22 H26 N2 O4 S	4.7E+02	7.7	2.7
Dipyridamol	58-32-2	DIP	504.64	C24 H40 N8 O4	8.2E+00	6.3	2.7
Disopyramide	3737-09-5	DIS	339.47	C21 H29 N3 O	4.5E+01	8.4	2.6
Enrofloxacin	93106-60-6	ENR	359.40	C19 H22 F N3 O3	3.4E+03	—	0.70
Erythromycin	114-07-8	ERY	733.95	C37 H67 N O13	1.4E+00	8.9	3.1
Ethenzamide	938-73-8	ETZ	165.19	C9 H11 N O2	4.5E+03	—	0.77
Fenoprofen	31879-05-7	FPF	242.28	C15 H14 O3	1.7E+02	7.3	3.9
Furosemide	54-31-9	FUR	330.75	C12 H11 Cl N2 O5 S	7.3E+01	3.9	2.0
Griseofulvin	126-07-8	GF	352.77	C17 H17 Cl O6	8.6E+00	—	2.2
Ibuprofen	15687-27-1	IBU	206.28	C13 H18 O2	2.1E+01	4.9	4.0
Ifenprodil	23210-56-2	IFP	800.99	C21 H27 N O2	2.6E+02	9.1, 9.7	3.9
Indomethacin	53-86-1	IND	357.79	C19 H16 Cl N O4	9.4E-01	4.5	4.3
Isopropylantipyrine	479-92-5	IPA	230.31	C14 H18 N2 O	3.0E+06	—	1.9
Ketoprofen	22071-15-4	KTP	254.29	C16 H14 O3	5.1E+01	4.5	3.1
Levofloxacin	100986-85-4	LVF	361.37	C18 H20 F N3 O4	—	5.5, 8.0	—
Lincomycin	859-18-7	LCM	443.00	C18 H34 N2 O6 S	9.3E+02	7.8	0.29
Mefenamic acid	61-68-7	MEF	241.29	C15 H15 N O2	2.0E+01	4.2	5.1
Metoprolol	51384-51-1	MTL	267.37	C15 H25 N O3	—	9.7	—
Nalidixic acid	389-08-2	NDA	232.24	C12 H12 N2 O3	1.0E+02	6.0	1.6
Naproxen	22204-53-1	NAP	230.26	C14 H14 O3	1.6E+01	4.2	3.2
Norfloxacin	70458-96-7	MFX	319.34	C16 H18 F N3 O3	1.8E+05	6.3, 8.8	-1.0
Oxytetracycline	79-57-2	OXT	460.44	C22 H24 N2 O9	3.1E+02	3.3, 7.3, 9.1	-0.90
Pirenzepine	28797-61-7	PIR	351.41	C19 H21 N5 O2	1.7E+01	1.8, 7.9	—
Primidone	125-33-7	PRI	218.25	C12 H14 N2 O2	5.0E+02	—	0.91
Propranolol	318-98-9	PPL	295.81	C16 H21 N O2	6.2E+01	9.4	0.74
Roxithromycin	80214-83-1	ROX	837.07	C41 H76 N2 O15	1.9E-02	—	2.8
Salbutamol	18559-94-9	SAL	239.31	C13 H21 N O3	1.4E+04	10	0.64
Sulfadimethoxine	122-11-2	SDMX	310.33	C12 H14 N4 O4 S	3.4E+02	2.1, 6.1	1.6
Sulfadimizine	57-68-1	SDM	278.32	C12 H14 N4 O2 S	1.5E+03	2.1, 7.5	0.89
Sulfamerazine	127-79-7	SMR	264.30	C11 H12 N4 O2 S	2.0E+02	2.1, 6.9	0.14
Sulfamethoxazole	723-46-6	SMZ	253.28	C10 H11 N3 O3 S	6.1E+02	1.9, 5.6	0.89
Sulfamonomethoxine	1220-83-3	SMM	298.32	C11 H12 N4 O3 S	4.0E+03	—	0.70
Sulfapyridine	144-83-2	SP	249.29	C11 H11 N3 O2 S	2.7E+02	2.7, 8.3	0.35
Sulfathiazole	72-14-0	STZ	255.32	C9 H9 N3 O2 S2	3.7E+01	2.5, 7.0	0.05
Sulpiride	15676-16-1	SLP	341.43	C15 H23 N3 O4 S	2.3E+03	9.1	0.57
Tetracycline	64-75-5	TC	480.90	C22 H24 N2 O8	2.3E+02	3.3, 7.7, 9.7	-3.7
Theophylline	58-55-9	TPL	180.16	C7 H8 N4 O2	7.4E+03	8.8	-0.02
Thiamphenicol	15318-45-3	TAP	356.23	C12 H15 Cl2 N O5 S	1.2E+04	7.2	-0.33
Tiamulin	55297-95-5	TL	493.76	C28 H47 N O4 S	7.0E-01	7.6	4.8
Triclocarban	101-20-2	TCC	289.54	C13 H9 Cl3 N2 O	2.4E-02	13	4.9
Triclosan	3380-34-5	TRI	289.54	C12 H7 Cl3 O2	1.0E+01	7.9	4.8
Trimethoprim	738-70-5	TMP	290.32	C14 H18 N4 O3	4.0E+02	7.1	0.91
Tylosin	1401-69-0	TYL	916.10	C46 H77 N O17	5.0E+00	7.7	1.6

—: no data

3.2.2 Treatment methods in STPs

Table 3.3 Summary of information on six STPs included in this study

	Area	Population	Biological treatment※	Disinfection	Operation capacity (m^3/day)	Septic tank (m^3/day)	Livestock waste (m^3/day)	Actual treatment volume (m^3/day)
A	Seoul	1,799,780	MLE	Chlorination	1,000,000	4,412	-	620,897
B	Seoul	3,204,179	MLE/CAS	Chlorination	2,000,000	2,850	-	1,661,500
C	Seoul	3,321,819	A2O/CAS	O3/Chlorination	1,710,000	3,639	-	1,344,338
D	Seoul	2,202,997	MLE	Sodium hypochlorite	900,000	40	-	793,618
E	Gyeonggi	70,959	MLE	UV	25,000	26	-	25,729
F	Gyeonggi	109,300	B3	Chlorination	48,000	101	308	40,573

※ MLE : Modified Ludzack- Ettinger process / CAS : Conventional Activated Sludge process / B3 : Bio Best Bacillus process

In the research area, there are six STPs (A to F). STPs A, B, C, and D are located in Seoul, and the STPs E and F are located in Gyeonggi-do (Figure 3.1). STPs A, B, D, and E use the Modified Ludzack-Ettinger (MLE) process, and STP-C uses the Anaerobic Anoxic Aerobic (A2O)/Conventional Activated Sludge (CAS) process. MLE process consists of the modification of a conventional activated sludge process where an anoxic zone is created or added upstream of the aerobic zone. The process uses an internal recycle that carries nitrates created in the nitrification process in the aerobic zone along with the mix liquor to be mixed in the influent to the anoxic zone. The STP-F treats wastewater through the Bio Best Bacillus (B3) process, and this is the only plant treating livestock wastewater as well (Table 3.3). There are combined and separated systems of sewerage in Seoul, while in Gyeonggi-do most apply separated sewerage except partially combined. All STPs are treating human night soil by collecting them using sewerage or a car. The each effluent is disinfected with chlorination, sodium hypochlorite, ozone, or UV disinfection. The detailed processes of the STPs are shown in Figure 3.2. MLE process of A, B, D and E STPs consists of the modification of a conventional activated sludge process where an anoxic tank is created or added upstream of the aerobic tank. The process uses an internal recycle that carries nitrates created in the nitrification process in the aerobic tank along with the mix liquor to be mixed in the influent to the anoxic tank. The amount of nitrates potentially removed in the anoxic tank depends on the recycle flow and availability of influent BOD. Next, A2O process of STP-C removes biological phosphorus along with simultaneous nitrification-denitrification. In the process, ammonia will be transformed into nitrite and then nitrate (nitrification) in the aerobic tank, and the return supernatant in the aerobic tank will be returned to the anoxic tank to proceed with denitrification. On the other hand, phosphate is released in the anaerobic tank, and then uptaken excessively in the later aerobic tank. Thus, phosphorus and nitrogen removal can be achieved

simultaneously in the A2O process. B3 process of STP-F is applied to accomplish a removal of nitrogen and phosphorus. When high-concentrated Bacillus sp. intakes nitrogen and phosphorus, it is composed to cells and then, denitrification is occurred and phosphorus is removed.

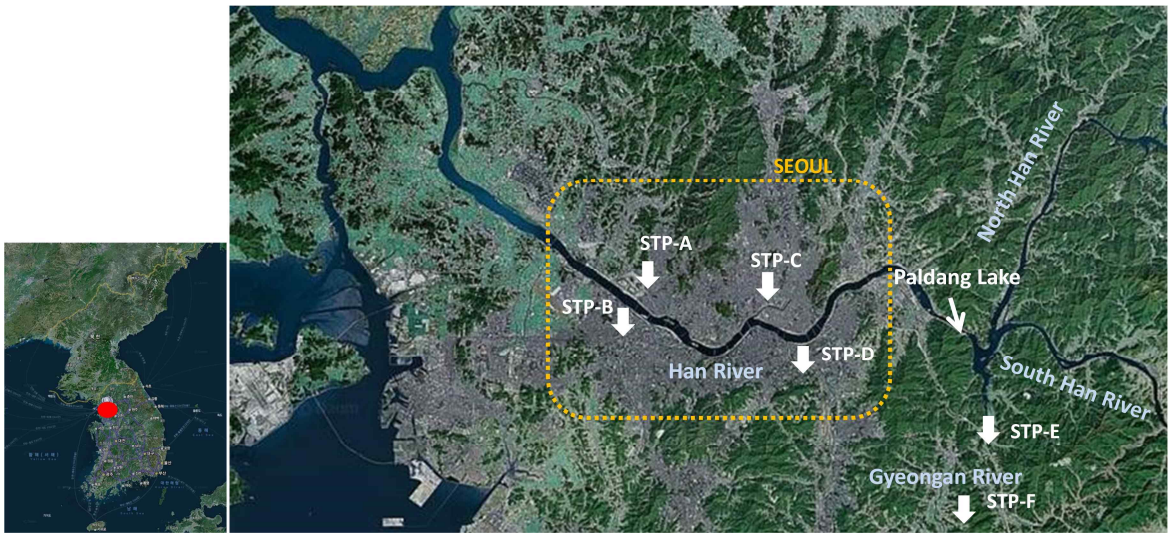


Figure 3.1 Location of the sewage treatment plants with rivers

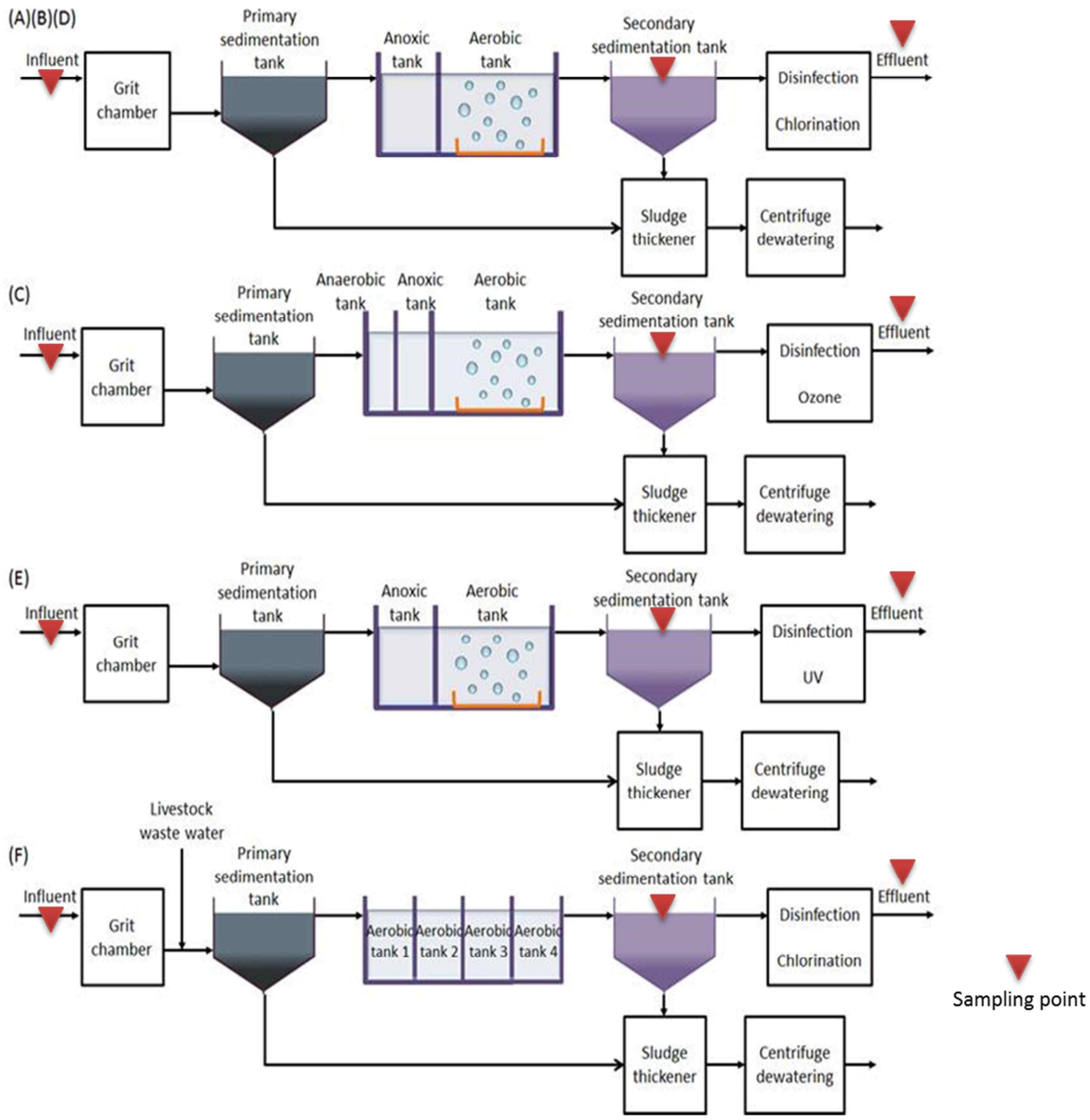


Figure 3.2 Characteristics of STPs located at the research area, (A), (B) and (D) are MLE process, (C) is A2O process, (E) MLE & UV process, and (F) B3 process.

3.2.3 Sampling and sample treatment

In this study, spot sampling of the effluent, secondary effluent, and influent of the STPs from 2011 to 2014 were conducted (Table 3.4).

Table 3.4 Sampling list of STPs and River

				2010	2011		2012			
				Oct	Aug	Nov	Jan	May	Aug	Nov
	Area	STPs	Sampling volume	Effluent, Secondary effluent, Final effluent - each 1000 mL, River - 2000 mL						
STPs	SEOUL	STP A	Effluent	-	Spot	Spot	Spot	Spot	Spot	Spot
			Secondary effluent	-	Spot	Spot	Spot	Spot	Spot	Spot
			Final effluent	-	Spot	Spot	Spot	Spot	Spot	Spot
		STP B	Effluent	-	Spot	Spot	Spot	Spot	Spot	Spot
			Secondary effluent	-	Spot	Spot	Spot	Spot	Spot	Spot
			Final effluent	-	Spot	Spot	Spot	Spot	Spot	Spot
		STP C	Effluent	Spot	-	Spot	Spot	Spot	Spot	Spot
			Secondary effluent	Spot	-	Spot	Spot	Spot	Spot	Spot
			Final effluent	Spot	-	Spot	Spot	Spot	Spot	Spot
		STP D	Effluent	-	Spot	Spot	Spot	Spot	Spot	Spot
			Secondary effluent	-	Spot	Spot	Spot	Spot	Spot	Spot
			Final effluent	-	Spot	Spot	Spot	Spot	Spot	Spot
	GYEONGGI-DO	STP E	Effluent	-	-	Spot	Spot	Spot	Spot	Spot
			Secondary effluent	-	-	Spot	Spot	Spot	Spot	Spot
			Final effluent	-	-	Spot	Spot	Spot	Spot	Spot
		STP F	Effluent	-	Spot	Spot	Spot	Spot	Spot	Spot
			Secondary effluent	-	Spot	Spot	Spot	Spot	Spot	Spot
			Final effluent	-	Spot	Spot	Spot	Spot	Spot	Spot
River		Gyoengan River	8 points	Spot	Spot	Spot	Spot	Spot	Spot	Spot

				2013				2014	
				Feb	May	Aug	Nov	Jan	Mar
	Area	STPs	Sampling volume	Effluent, Secondary effluent, Final effluent - each 1000 mL, River - 2000 mL					
STPs	SEOUL	STP A	Effluent	Spot	Spot & Comp.	Spot	Spot	-	-
			Secondary effluent	Spot	Spot & Comp.	Spot	Spot	-	-
			Final effluent	Spot	Spot & Comp.	Spot	Spot	-	-
		STP B	Effluent	Spot	Spot	Spot & Comp.	Spot	-	-
			Secondary effluent	Spot	Spot	Spot & Comp.	Spot	-	-
			Final effluent	Spot	Spot	Spot & Comp.	Spot	-	-
		STP C	Effluent	Spot	Spot	Spot	Spot & Comp.	-	-
			Secondary effluent	Spot	Spot	Spot	Spot & Comp.	-	-
			Final effluent	Spot	Spot	Spot	Spot & Comp.	-	-
		STP D	Effluent	Spot	Spot	Spot	Spot	-	-
			Secondary effluent	Spot	Spot	Spot	Spot	-	-
			Final effluent	Spot	Spot	Spot	Spot	-	-
	GYEONGGI-DO	STP E	Effluent	Spot & Comp.	Spot & Comp.	Spot & Comp.	Spot & Comp.	Spot	Spot
			Secondary effluent	Spot & Comp.	Spot & Comp.	Spot & Comp.	Spot & Comp.	Spot	Spot
			Final effluent	Spot & Comp.	Spot & Comp.	Spot & Comp.	Spot & Comp.	Spot	Spot
		STP F	Effluent	Spot & Comp.	Spot & Comp.	Spot & Comp.	Spot & Comp.	Spot	Spot
			Secondary effluent	Spot & Comp.	Spot & Comp.	Spot & Comp.	Spot & Comp.	Spot	Spot
			Final effluent	Spot & Comp.	Spot & Comp.	Spot & Comp.	Spot & Comp.	Spot	Spot
River		Gyoengan River	8 points	Spot	Spot	Spot	Spot	Spot	Spot

A preliminary investigation was conducted at STP-C in Seoul and Gyeongan River in October 2010. Through this sampling, spots were selected with an earnest survey on Gyeongan River in cooperation with Seoul city set to from August 2011. However, due to the flood occurring in August 2011, it was impossible to investigate on STP-E. Then, from November 2011 through November 2012, the investigation was conducted for each season by spot sampling on four STPs of Seoul city, two STPs on Gyeonggi-do and at Gyeongan River. In February 2013, to ascertain the difference between, composite and spot samplings were simultaneously conducted at each of STPs. Our study used the investigation made through November 2013 for Seoul city and through March 2014 for Gyeongan River basin. Thereafter, the differences in concentrations of the PPCPs and estrogens according to the sampling method were checked, and the appropriate sampling method was reviewed. Reason for the comparison was to confirm the stability of PPCPs and estrogens. The sample bottles were first rinsed twice with the sample water before 500-1000 mL was collected. Immediately, 1 g L^{-1} ascorbic acid was added and the bottles were stored in cooling box during their transport back to our laboratory. In the laboratory, the samples were filtered through GF/B glass fiber filter (1 μm pore size, Whatman, UK). After filtration PPCPs, 1 gL^{-1} EDTA-2Na and surrogate (41 mixed, 1 ppm 50 μL) were added and solid phase extraction (SPE) with Oasis HLB (200 mg, 6 cc; 30 μm partial size, Waters) cartridges was carried out at a flow rate of 10 mL min^{-1} (no more than 4hr after sample collection). For estrogens sample, pH was adjusted to 3-4 with 20 %

acetic acid. After injection of surrogate (7 mixed, 1 ppm 50 μL), this was concentrated in Oasis HLB (200 mg, 6 cc; 30 μm partial size, Waters) cartridge using a concentrator. After concentration, cartridge was dried for over 2 hours to make an eruption test. Elution of free estrogens was made using Oasis HLB and NH2 (360 mg, Aminopropyl, 55–105 μm partial size, Waters) cartridges together by 8 mL MeOH. The PPCPs on the cartridge were eluted from the cartridge by 6 mL MeOH. The eluent solvent extract was evaporated to dryness by a gentle stream of nitrogen gas. The residue of PPCPs was dissolved in 1 mL of 0.1 % formic acid– MeOH mixture (85/15, v/v) and the residue of Estrogens was dissolved in 1 mL of acetonitrile and Milli Q (1:9) solution.

3.2.4 LC/MS/MS analysis

Waters ACQUITY UPLC system (Waters) equipped with ACQUITY Bridged Ethyl Hybrid (BEH) C18 column (1.7 μm, 2.1 mm × 100 mm), and Quattro micro API mass spectrometer (Waters) were used (Okuda et al., 2009; Narumiya et al., 2013). For estrogens, ACQUITY UPLC BEH C8 columns (1.7 μm, 2.1 mm × 100 mm) were used (Vimal et al., 2009). The method of PPCPs and estrogens using the recovery correction which was calculated from the difference between two aliquots from one sample with and without addition of target PPCPs mixture, and the internal standard method using appropriate surrogate standards were used for the quantification for the samples.

3.2.5 Data analysis

The removal efficiency of PPCPs and estrogens in whole treatment of STPs was calculated by the following equation.

$$\{(Con_{In} - Con_{Fe})/Con_{In}\} \times 100 \quad eq1$$

where Con_{In} is concentration of influent, Con_{Fe} is concentration of final effluent of PPCPs and estrogens. The removal efficiency in the primary settling and biological treatment can be calculated, as follows:

$$\{(Con_{In} - Con_{Se})/Con_{In}\} \times 100 \quad eq2$$

where Con_{Se} is concentration of secondary effluent of PPCPs and estrogens. So, removal efficiency in the disinfection was calculated by the following equation.

$$\{(Con_{Se} - Con_{Fe})/Con_{Se}\} \times 100 \quad eq3$$

Of the analysis results, only the data of which the signal to noise (S/N) ratios ≥ 3 and the recovery rate of the surrogate over 30 % were used in order to increase the accuracy of the data.

Lastly, concentrations estimated for STP with PPCPs use were calculated using the expression below.

$$\text{Predicted concnetration} = P\, M_h\, (1 - L_h) / Q_{In} \qquad eq4$$

The PPCPs and estrogens concentrations in wastewater in target STP were predicted from the annual consumption (M_h, kg/person-year), the number of inhabitants served (P), human loss of compounds (L_h) and Q_{In} flow rate of sewage influent (m^3/day).

3.3 Results and discussion

3.3.1 Comparison of composite and spot sampling

A composite sampler was installed in the STPs, the sampling was conducted 4 times (February 2013 ~ November 2013) with an interval of 2 hours, and the spot sampling was conducted during the composite sampling at the same points. Thereafter, the concentrations of PPCPs and estrogens in the composite samples and the spot samples were compared, and the result is shown in Figure 3.3.

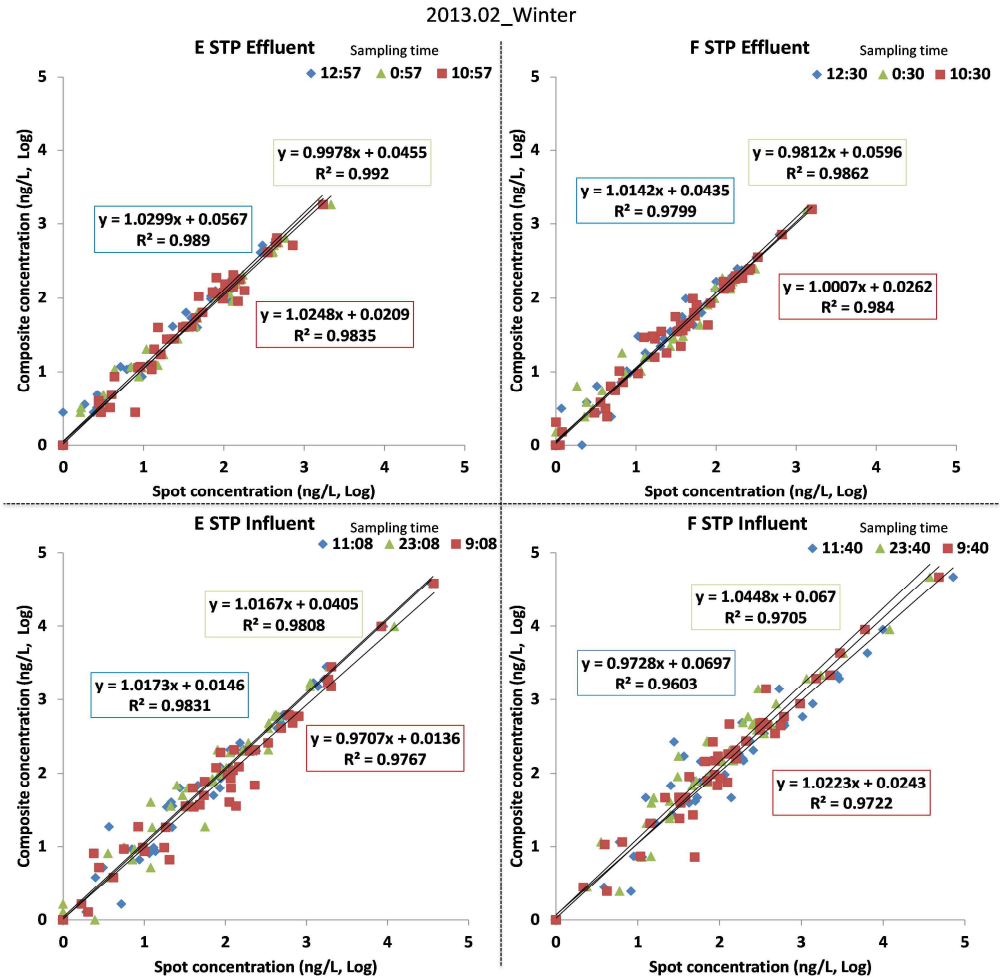


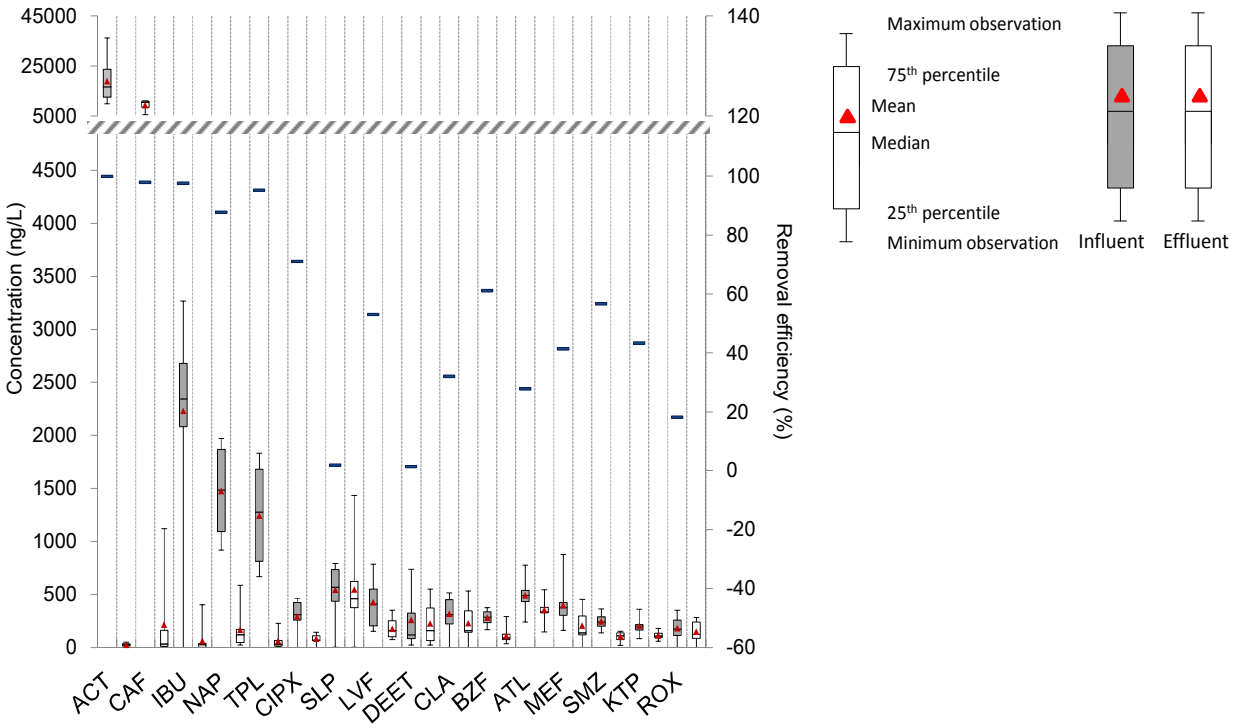
Figure 3.3 Correlations on the detection of PPCPs and estrogens by sampling method at STP E and F

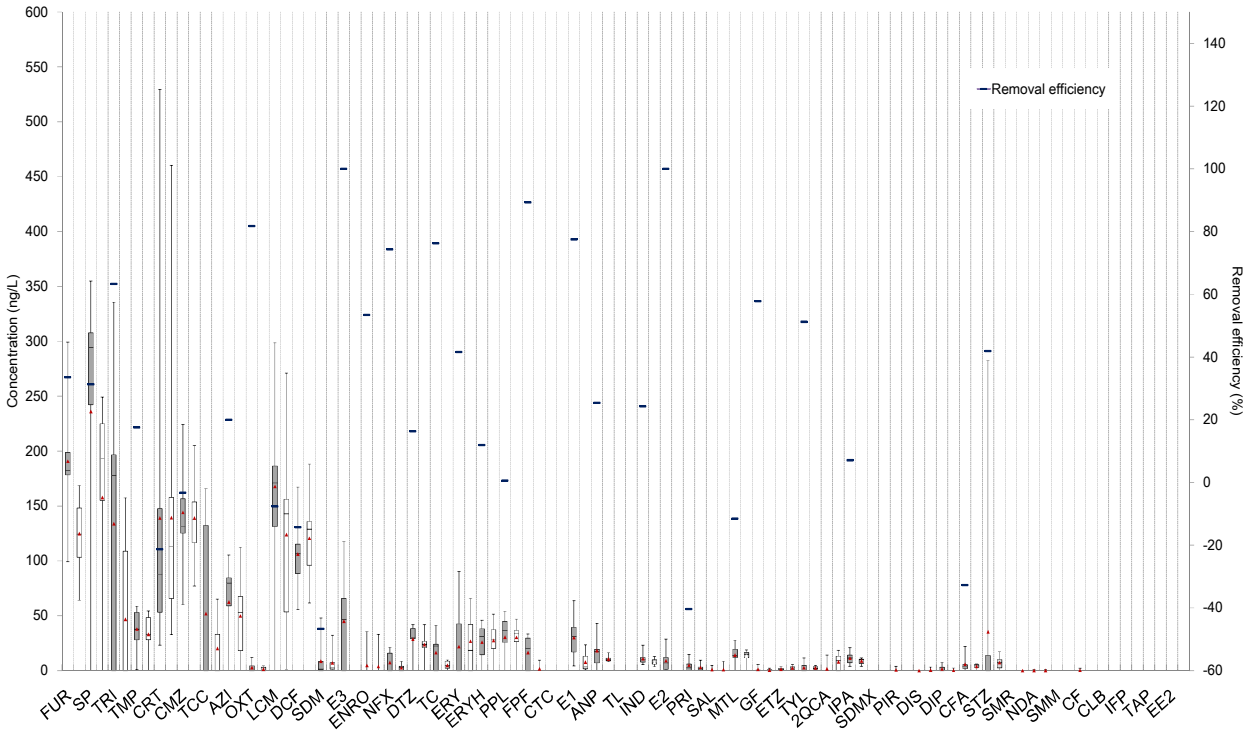
Concentration of Spot sampling on horizontal axis shows concentration immediately after installation (blue), 12 hours later (green) and 22 hours later (red), while concentration of composite sampling on vertical axis is the concentration mixed with a 24-hour collected sample in consideration of flow rate. Figure 3.2 shows the result of installing in February 2013 with graphs in comparison for other seasons displayed in Appendix A. From these results, it can be inferred that the coefficient of determination (R) of the composite and spot samples of the effluent and influent was over 0.96, which indicates high correlation. Thus, in this study, the data was analyzed using the data of spot samplings.

3.3.2 Overall concentrations and removal efficiency of PPCPs and estrogens in STPs

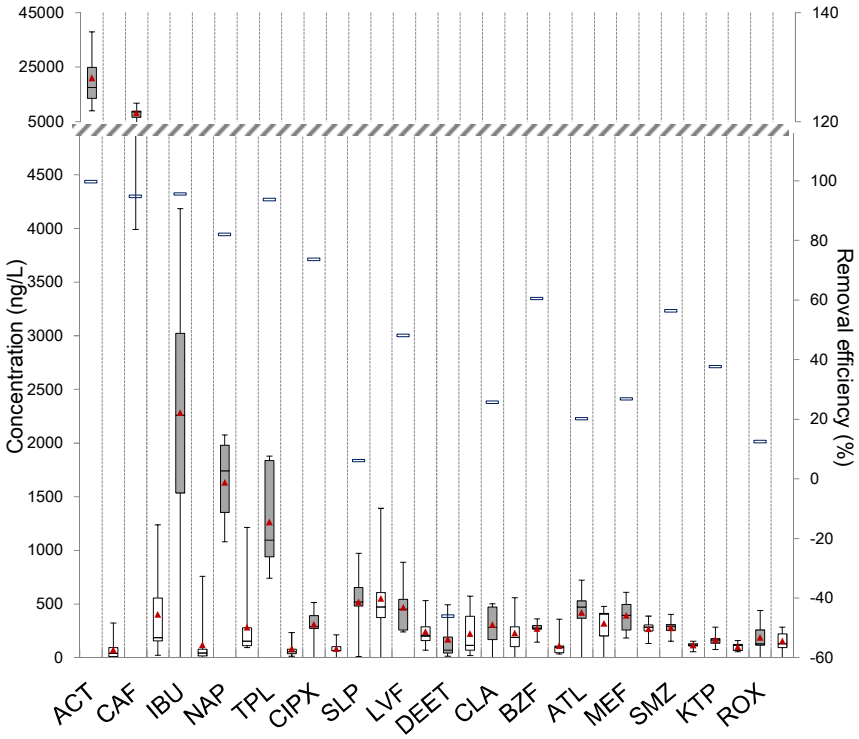
The concentrations of PPCPs and estrogens detected in the six STPs between August 2011 and January 2014 are show in Figure 3.4. This figure is box plots displaying 25th, median and 75th percentiles as boxes, and minimum and maximum concentrations, as line, red triangle (average concentration) and blue bar (removal efficiency), respectively. All of the influent in STPs shows high concentrations of acetaminophen, caffeine, ibuprofen, naproxen, theophylline, ciprofloxacin, sulpiride, levofloxacin, DEET, clarithromycin, bezafibrate, atenolol, mefenamic acid, sulfamethoxazole, ketoprofen, and roxithromycin. From STP-A (influent) DEET (260 ng/L) showed the highest concentration and from STP-C (influent) caffeine (9,549 ng/L), bezafibrate (343 ng/L) and ketoprofen (235 ng/L) were detected in the highest concentration. From STP-E (influent), ciprofloxacin (1,136 ng/L), levofloxacin (1,102 ng/L), clarithromycin (637 ng/L) and roxithromycin (400 ng/L) and from STP-F (influent), acetaminophen (50,091 ng/L), ibuprofen (3,138 ng/L), naproxen (2,222 ng/L), theophylline (2,173 ng/L), sulpiride (1,013 ng/L), atenolol (622 ng/L), mefenamic acid (467 ng/L) and sulfamethoxazole (542 ng/L) were the substances detected in the highest concentration with the largest number. STPs A, B, C and D are located in Seoul, which treat wastewater and excretions occurring in Seoul. As these STPs treat the wastewater occurring in Seoul, there was no big difference in concentrations between PPCPs and estrogens detected from the influent. STP E and F are located in Gyeonggi-do, while STP-E treating sewage and excrements, STP-F is treating livestock wastewater with domestic wastewater. Consequently, concentrations of sulfadimidine, chlortetracycline, sulfathiazole were observed higher than other STPs. However, with low removal efficiency at STP-F, sulfadimidine and sulfathiazole were detected in a similar concentration in effluent. In the STP-F, where livestock wastewater is also treated, sulfadimidine and chlortetracycline were detected in high concentrations.

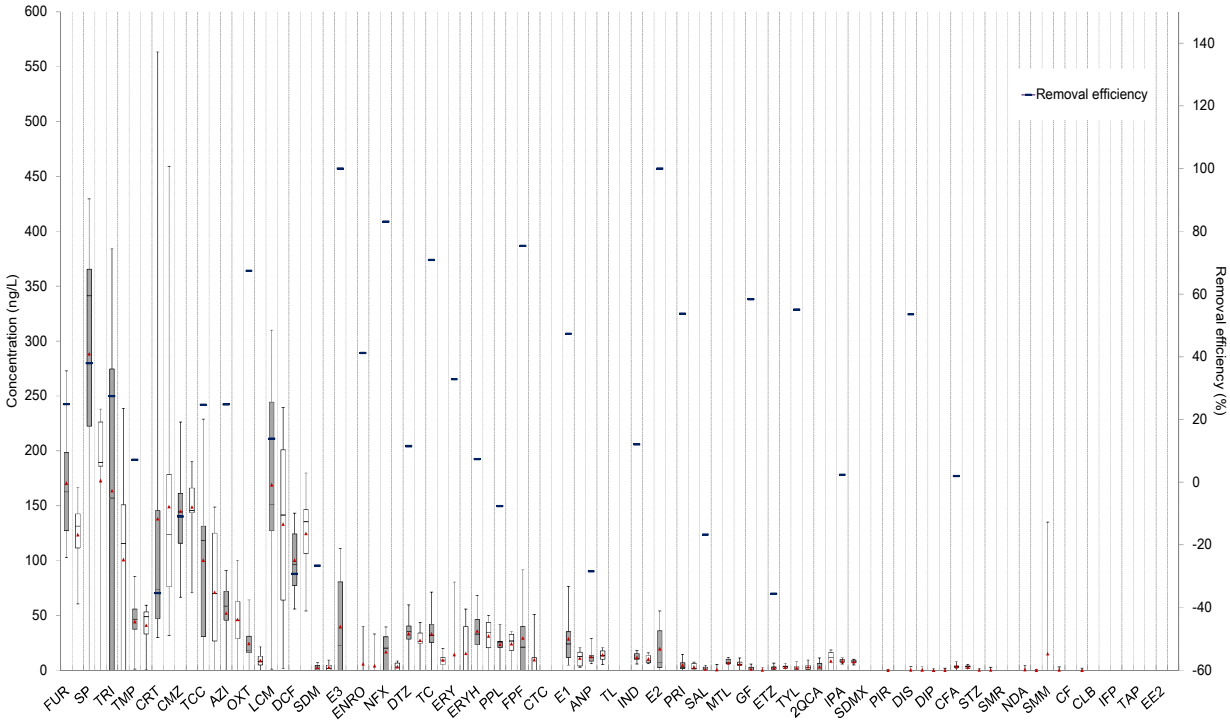
1. STP-A (2011.10 ~ 2013.08, n=10)



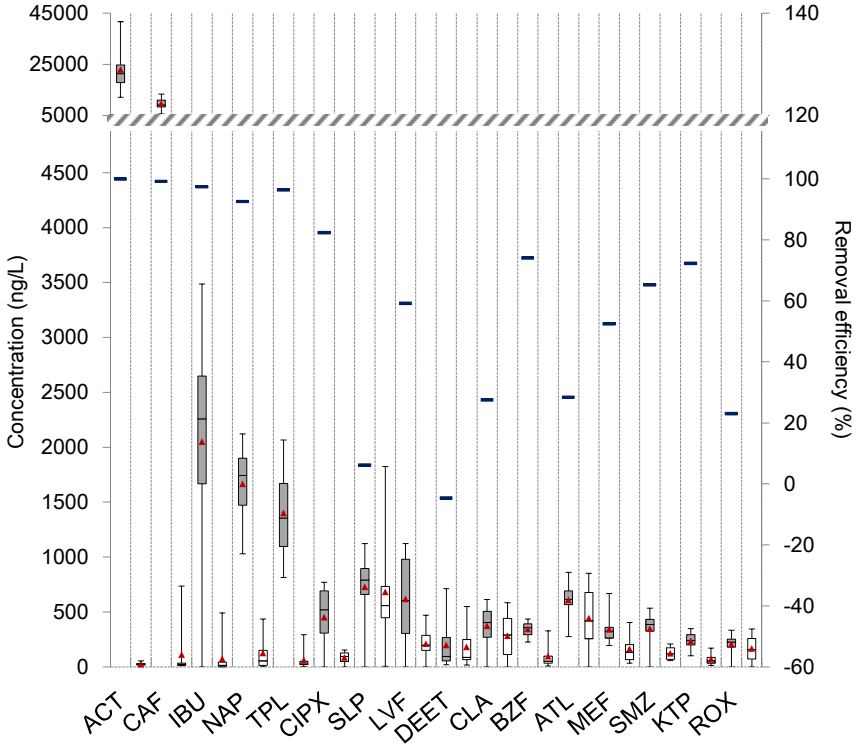


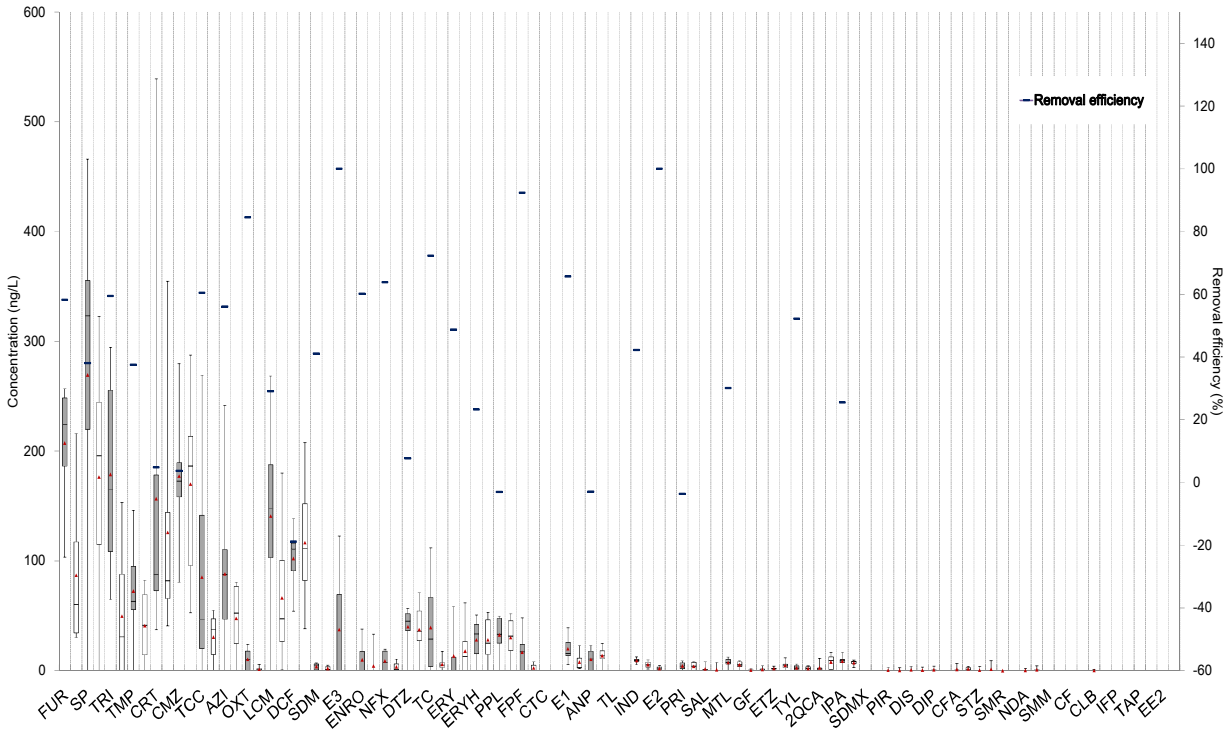
2. STP-B (2011.10 ~ 2013.08, n=10)



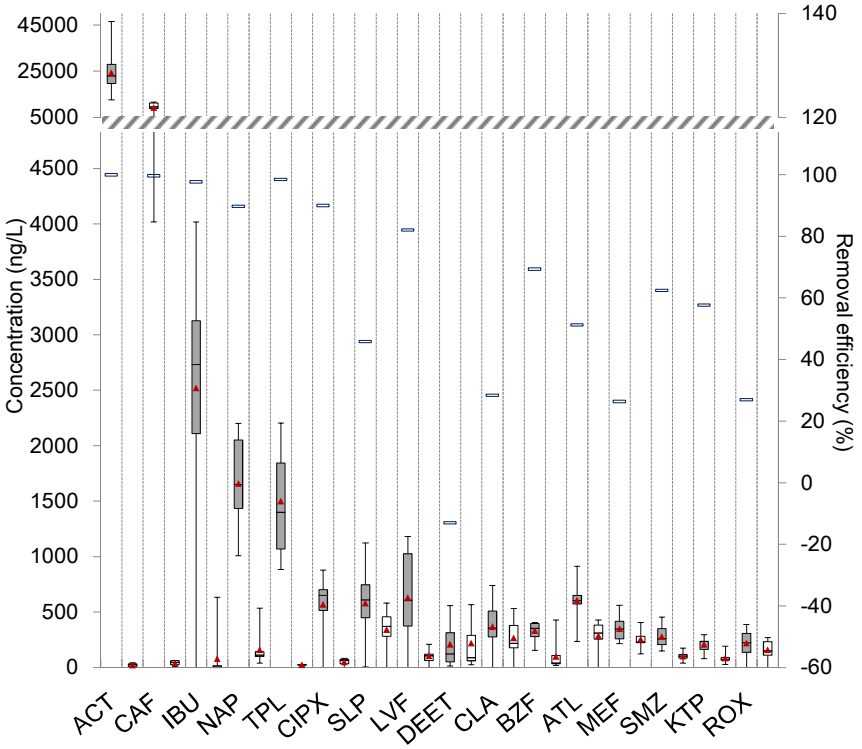


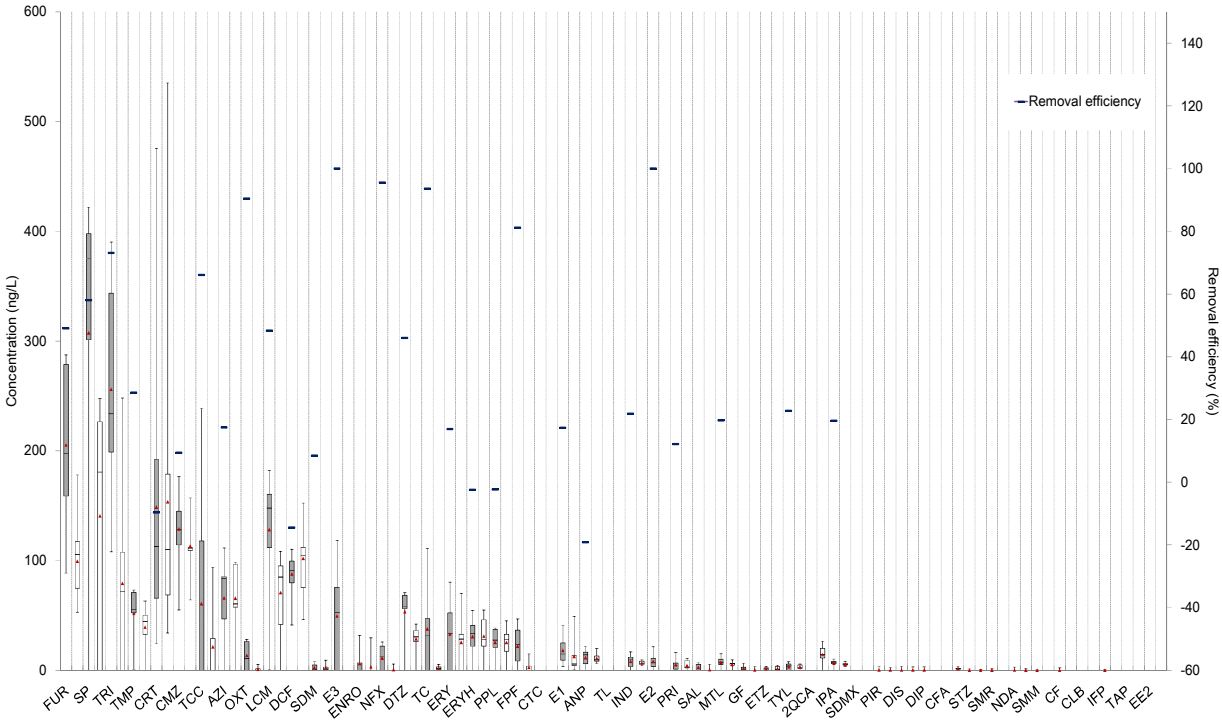
3. STP-C (2011.10 ~ 2013.08, n=10)



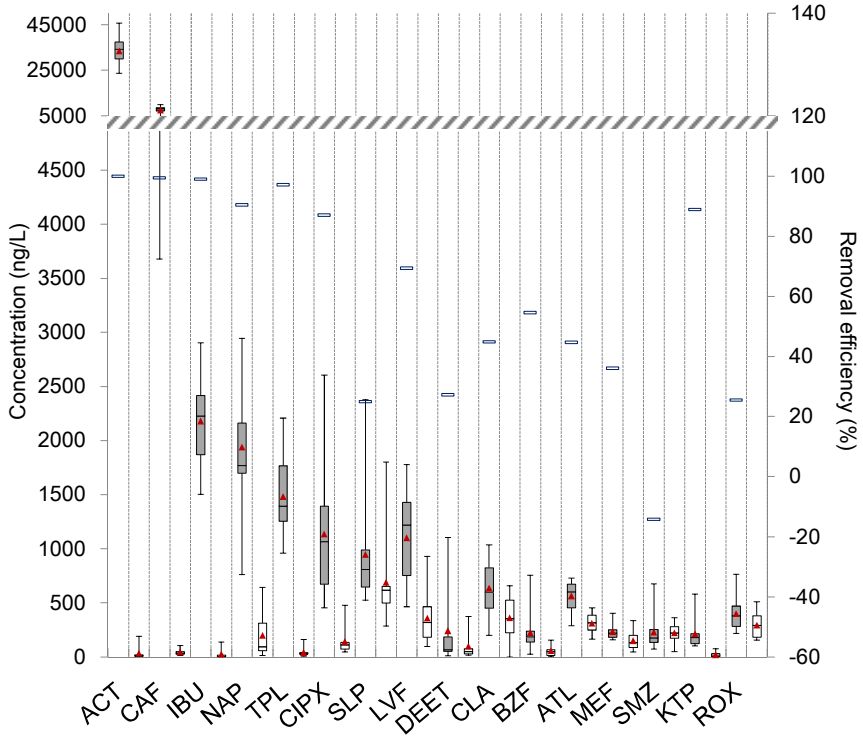


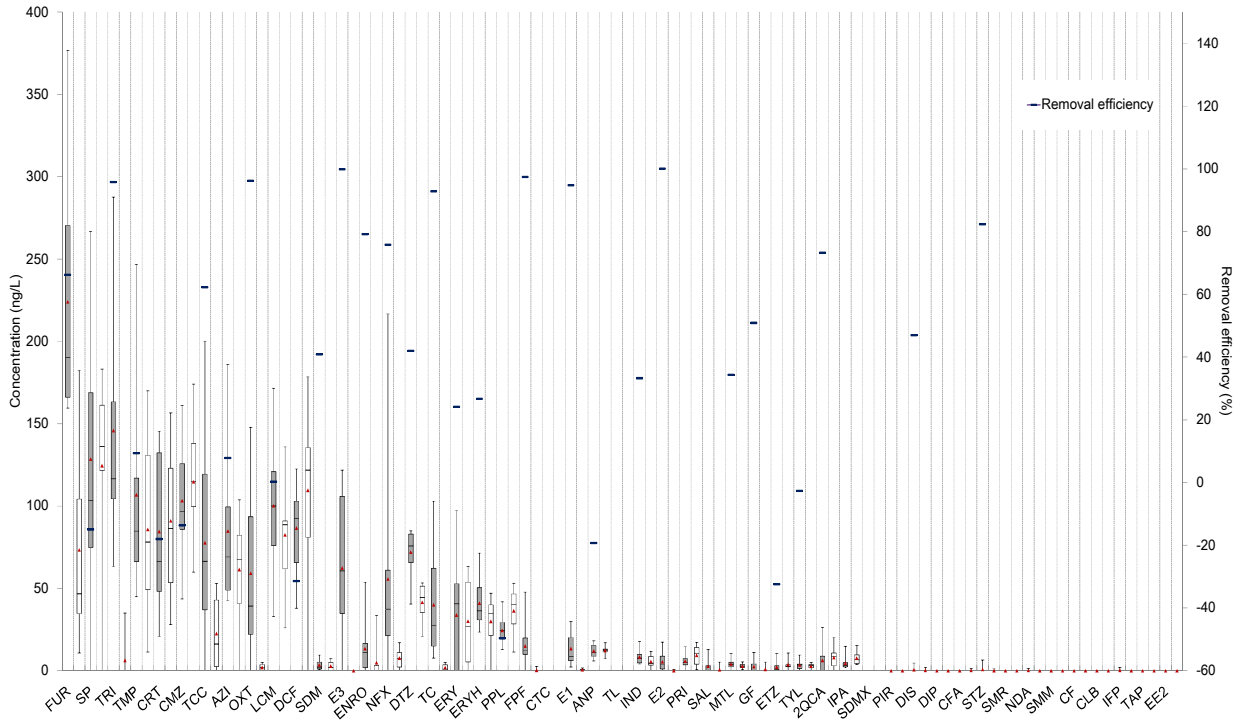
4. STP-D (2011.10 ~ 2013.08, n=10)





5. STP-E (2011.10 ~ 2014.01, n= 11)





6. STP-F (2011.10 ~ 2014.01, n=11)

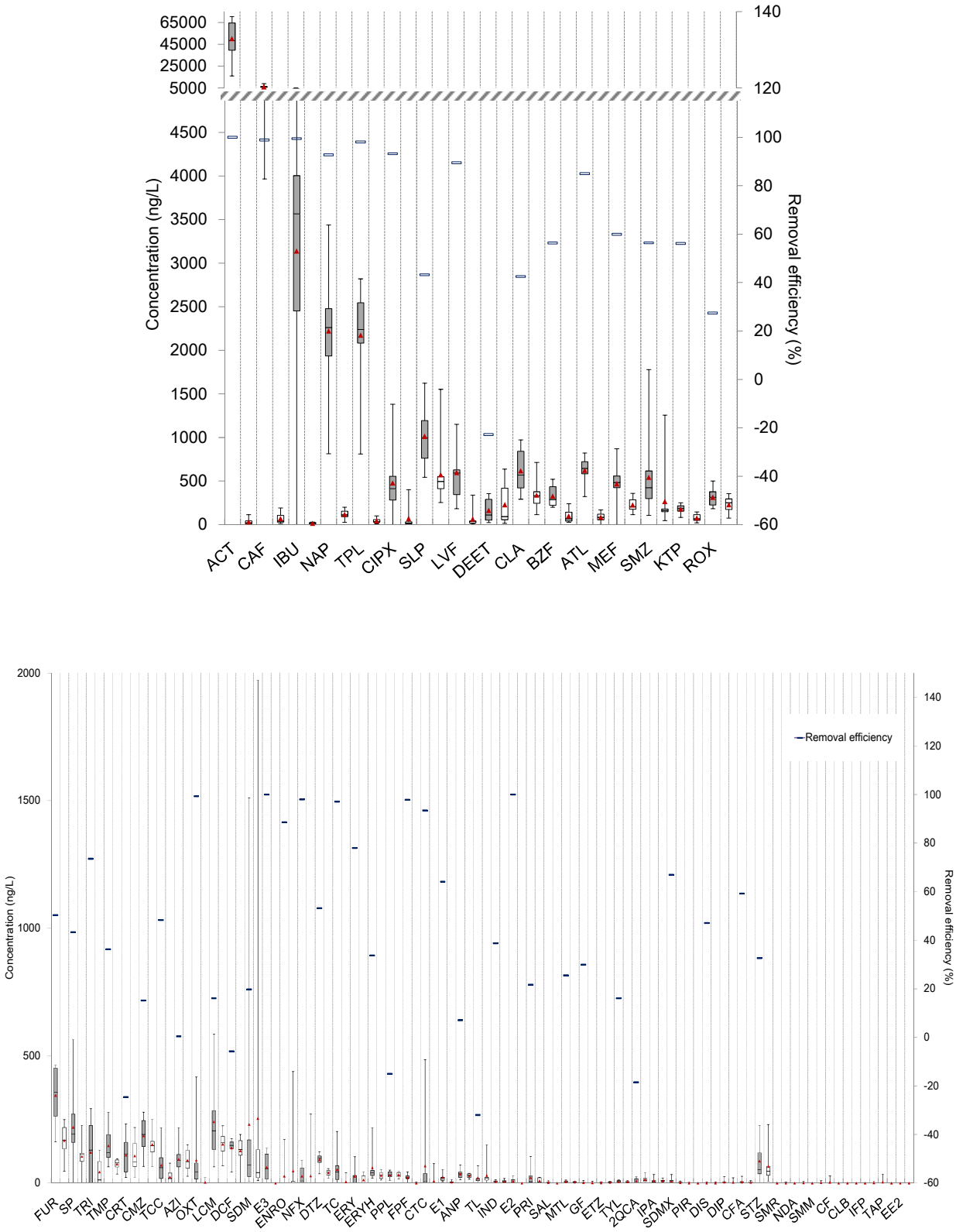


Figure 3.4 Concentration of PPCPs and estrogens and removal efficiency of each substance detected in influent and effluent at STPs of the area of research

3.3.2.1 Seasonal specific

PPCPs and estrogens are coming into STPs located at study area together with diverse kinds of sewage. To confirm the characteristics of PPCPs and estrogens coming into each STP, it was verified how the loadings of 49 PPCPs and 3 estrogens remaining in influents change by season and put into Figure 3.5. In this study, data were used by division into spring (March - June), summer (July - September), autumn (October and November) and winter (December - February).

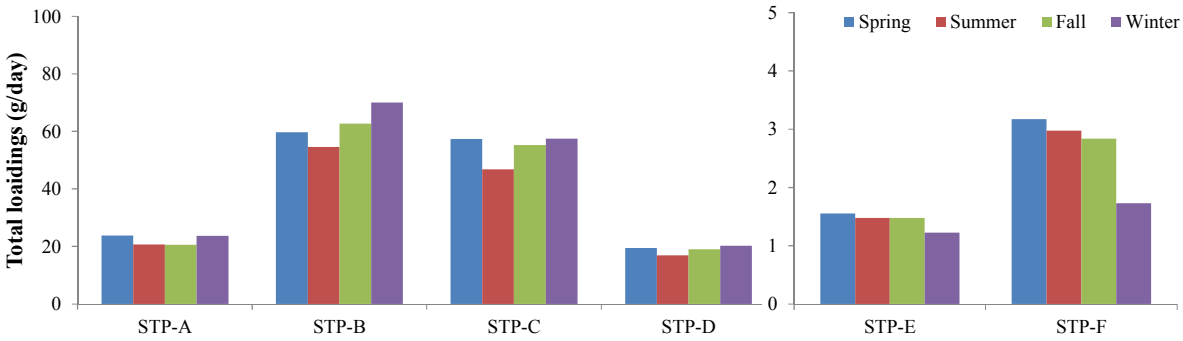


Figure 3.5 Total loading of PPCPs and estrogens measured in this study remaining in influents of STPs by change of season
(Limit of detection (LOD) was excluded from calculation assuming that it has not been detected.)

For STPs A, B, C and D, influent loadings were high in spring and winter but for STP E and F in spring. Among STPs in our study area, five (STPs A-E) are treating the sewage generated from humans waste and one STP F is livestock wastewater together with human-generated sewage. So Figure 3.6 shows the seasonal characteristics on loadings of selected PPCPs observed in the influent to STPs A to E.

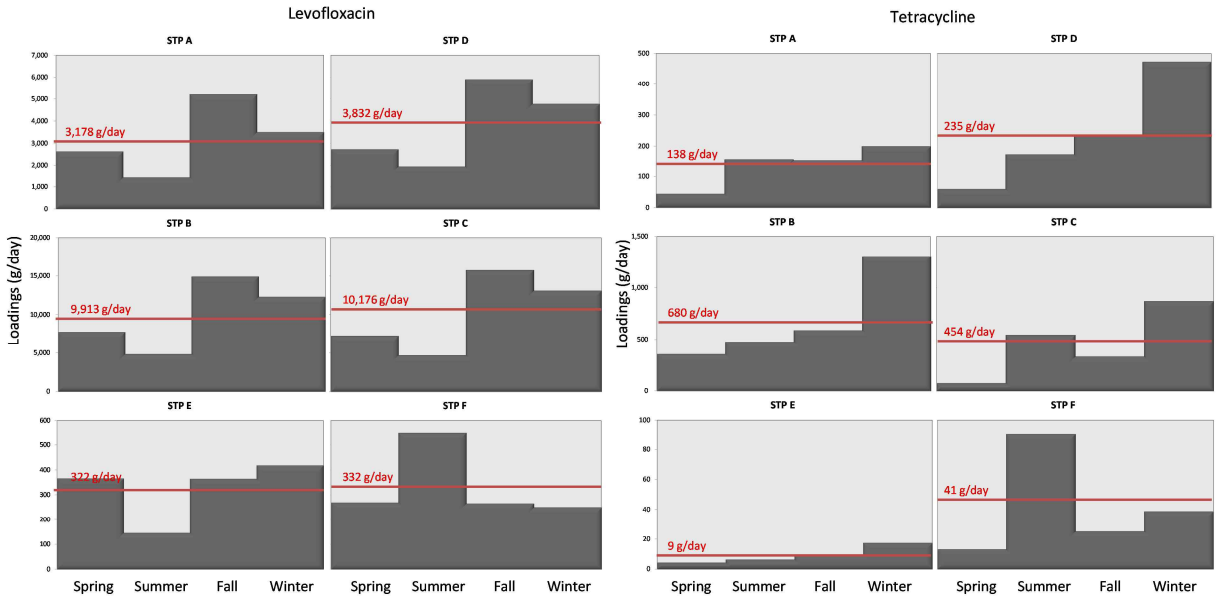
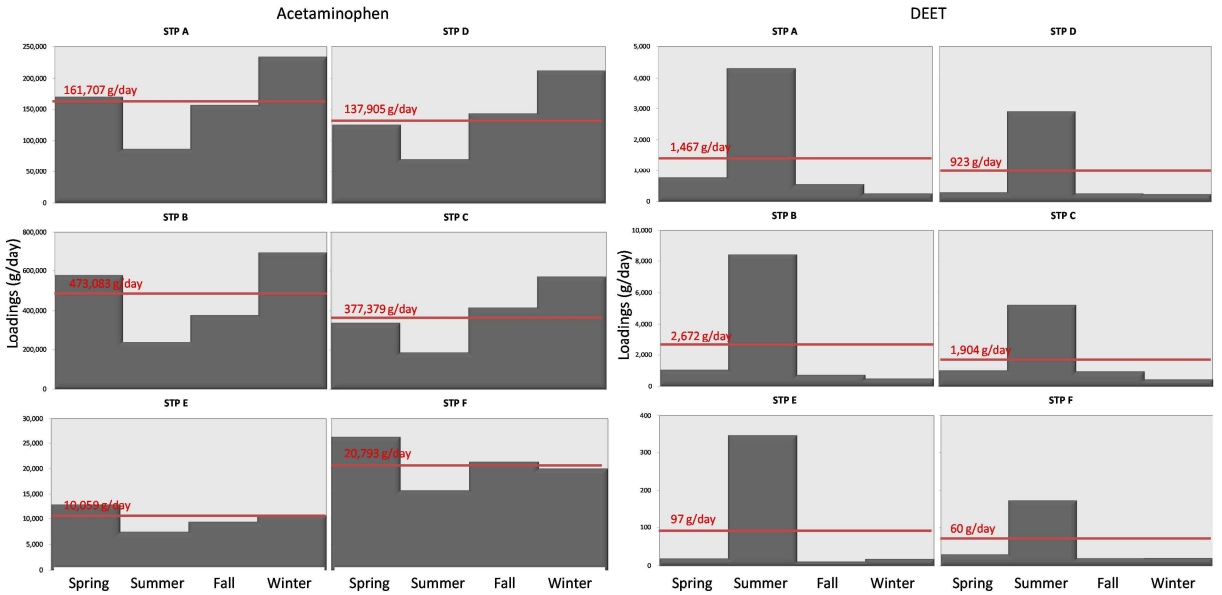


Figure 3.6 Seasonal characteristics of loadings of selected PPCPs in the influent sewage of STPs A to E

In the result of STP A-E, levofloxacin showed larger loadings in fall and winter but a larger loadings in summer was found in STP F which treats livestock wastewater. Levofloxacin, which is an antibiotic used by both man and livestock, showed higher loadings in the summer with high humidity and temperature that may come anthrax (Boxall et al., 2012). Tetracycline, which is another antibiotic, showed the characteristic of larger loadings in the summer while the other STPs for domestic wastewater show larger loadings in winter.



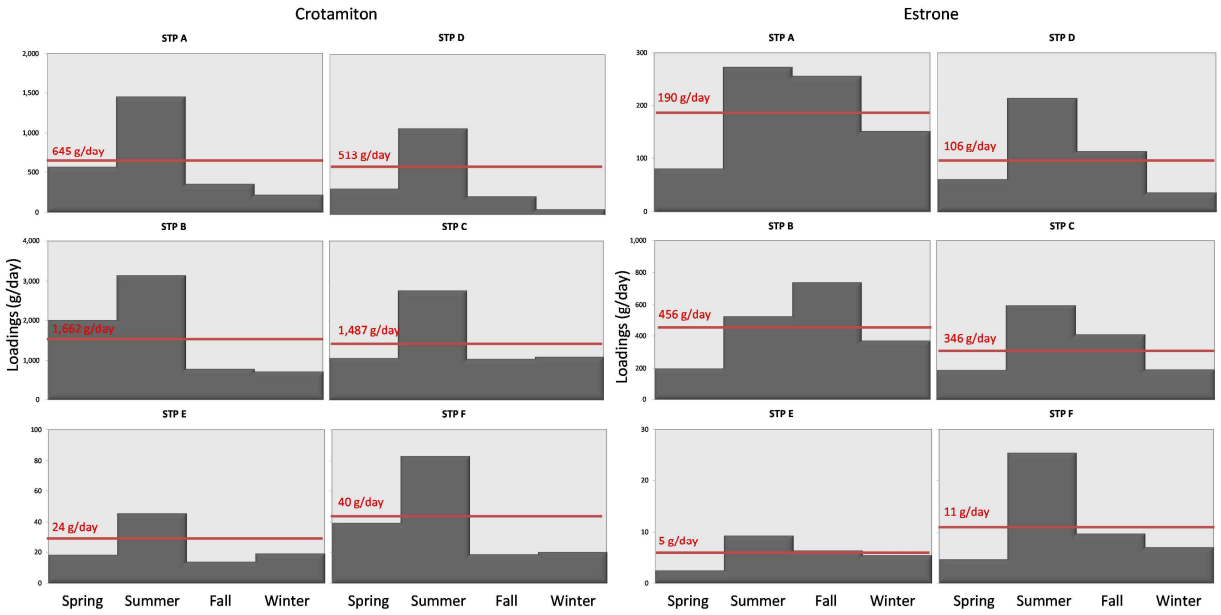


Figure 3.7 Characteristics of the loadings of selected PPCPs in the influent sewage of STPs A to E

Figure 3.7 shows selected PPCPs and estrogens with the similar seasonal characteristics for all the STPs. Acetaminophen showed a high component ratio in spring and winter in influents of all STPs because it is chiefly used for antifebrile in low temperatures. DEET and crotamiton showed larger loadings in summer because DEET is contained in insecticides much used in summer and crotamiton in medicine used for skin itchiness for mosquito or other reasons. Among estrogens, estrone showed a high component in summer and winter because other estrogens are converted from estradiol into estrone in seasons of high temperature (Vimal kumar et al., 2009).

3.3.2.2 Removal characteristics

We verified characteristics of inflow and outflow of PPCPs by diverse treatment process in our study area. Treatment process was divided into MLE/UV, MLE/Sodium hypochlorite, MLE/Chlorination, B3/Chlorination and A2O/Ozone and they were show in Figure 3.8 on the target of 12 substances in high concentration of detection.

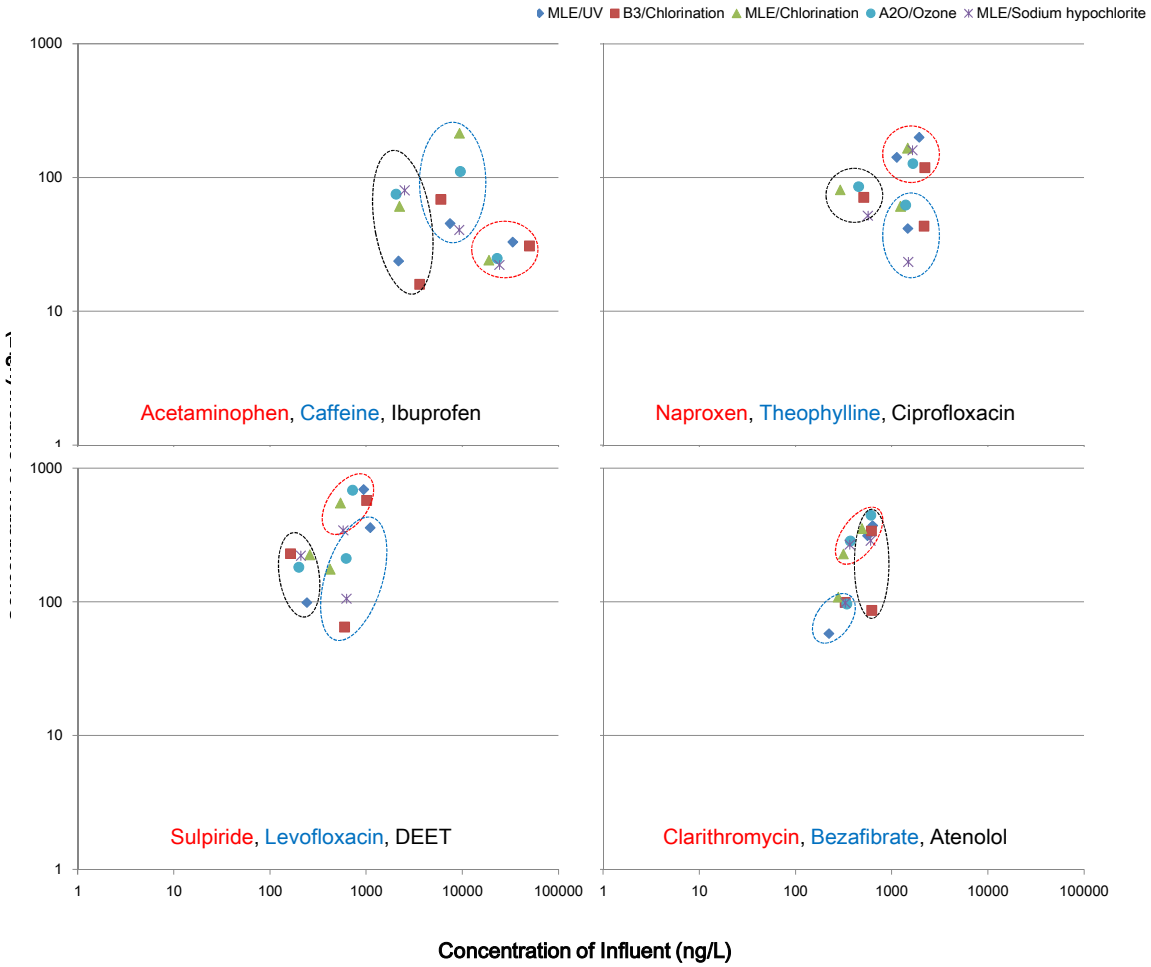


Figure 3.8 Concentrations of 12 substances in high concentration of detection remaining in influents and effluents by treatment process

For acetaminophen, naproxen, theophylline, ciprofloxacin, sulpiride, clarithromycin and bezafibrate, there were no big differences found by the process. However, caffeine showed the concentration of 214 ng/L in the effluent of MLE/Chlorination process, a higher concentration than other processes. Ibuprofen showed a low effluent in B3/Chlorination while a high effluent in MLE/Sodium hypochlorite and A2O/Ozone. Levofloxacin showed a lower effluent in B3/Chlorination, and so did DEET in MLE/UV, compared to other processes. Finally, Atenolol showed a low concentration in effluents of B3/Chlorination process. By treatment process, there was difference in the concentration of PPCPs remaining in effluents, with the exact characteristics of removal by treatment method discussed in 3.3.6 and 3.3.7.

3.3.3 Composition of PPCPs and estrogens in influent sewage in the STPs

In the research area, there are four STPs located in Seoul and two STPs located in Gyeonggi-do. The compounds detected were classified into NSAIDs, antibiotics, BLLAs, estrogens, and others.

The PPCPs and estrogens found in the influent are shown with populations connected to each STP in Figure 3.9.

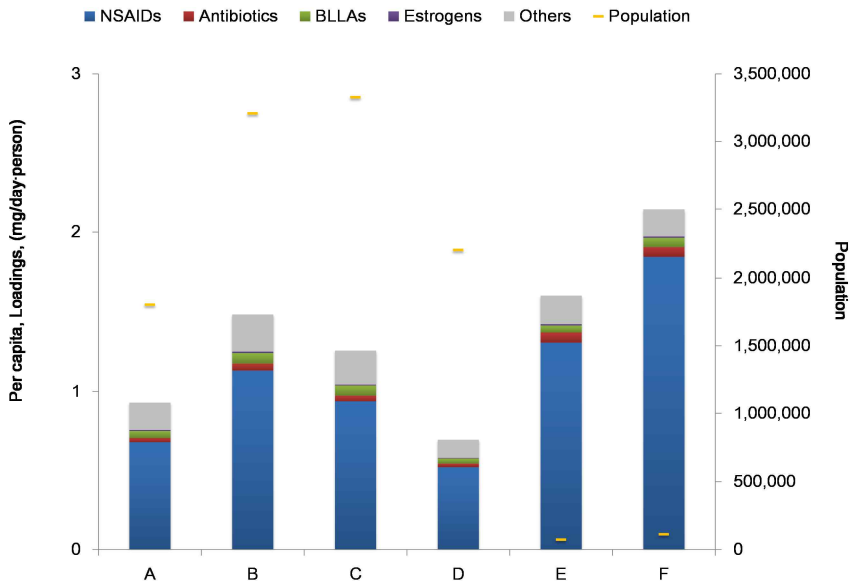


Figure 3.9 Composition of PPCPs and estrogens in influents at STPs of Korea in terms of per capita loadings
(STPs A, B, C and D are located in Seoul; STPs E and F in Gyeonggi-do, For LOD, LOQ excluded from calculation with assumption to have been undetected, we used the mean value during this study.)

The influent of all the STPs mainly contains NSAIDs, followed by antibiotics, BLLAs, and estrogens. Among the detected NSAIDs, acetaminophen, which is used as a fever reducer, ibuprofen and mefenamic acid, which are used as an anti-inflammatory pharmaceutical and a painkiller, and naproxen, which is an antiphlogistics for arthritis, show high concentrations. Among the antibiotics, ciprofloxacin is mainly used for the treatment of a number of bacterial infections; levofloxacin and roxithromycin, which are fluoroquinolone antibiotics, are used to treat tract, urinary and soft tissue infections; and sulfamethoxazole is commonly used to treat urinary tract infections. In case of the BLLAs, bezafibrate was detected, which is used to treating hyperlipidemias. In case of the estrogens, which are sex hormones, estrone, estradiol, and estriol were detected. Ethynylestradiol was not detected in any sample. The results of the comparison of the influents of the STPs located in Seoul and the influent of the STP-F, where livestock wastewater is treated, are shown in Figure 3.10. Influent was compared between domestic STPs and that treats livestock wastewater in combination to verify the characteristics of both.

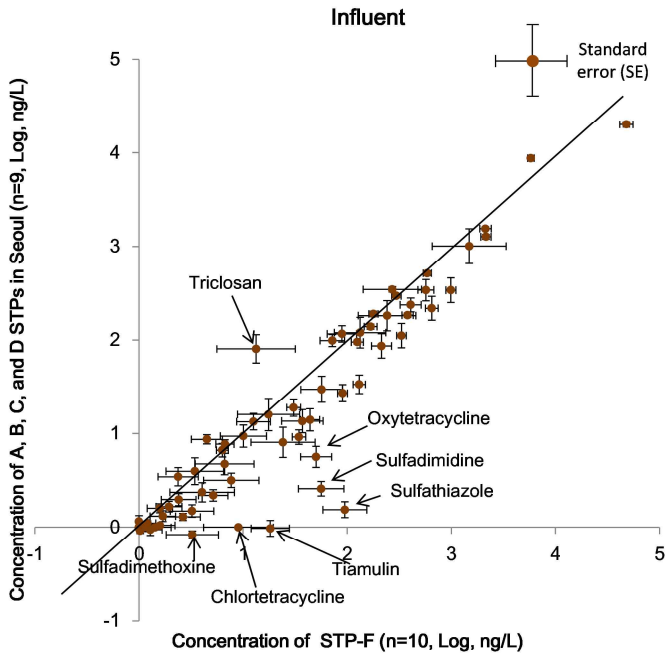


Figure 3.10 Comparison of PPCPs and estrogens concentration in influent into STP-F receving human and animal waste and these in Seoul for treatment

The PPCPs that was detected at a relatively high concentration in STPs of Seoul was triclosan, which is a substance that is often used as an antimicrobial agent in cosmetics. Tiamulin, chlortetracycline, and sulfadimethoxine were detected only in the STP-F. Oxytetracycline, sulfadimidine, and sulfathiazole are used by both humans and animals. Concentration at STP with use of PPCPs was measured in estimation using Equation 4. Concentrations of acetaminophen, atenolol, carbamazepine, ciprofloxacin, diltiazem, erythromycin, ibuprofen, mefenamic_acid, naproxen, roxithromycin, sulfamethoxazole and tetracycline were estimated (Figure 3.11) with production volume, human loss and usage per capita shown in Table 3.4 (MEK 2008).

Table 3.5 Production amount, human loss and excreted per capita of the selected PPCPs in Korea

Compounds	Production amount (kg)	Human loss (L_h)	Excreted Per Capita (kg/year)
Acetaminophen	765,730	0.80	15.19
Atenolol	12,344	0.10	0.24
Carbamazepine	8,997	0.75	0.18
Ciprofloxacin	12,106	0.25	0.24
Diltiazem	7,070	0.50	0.14
Erythromycin	57,670	0.60	1.14
Ibuprofen	145,849	0.87	2.89
Mefenamic_acid	51,014	0.48	1.01
Naproxen	69,274	0.90	1.37
Roxithromycin	6,447	0.10	0.13
Sulfamethoxazole	12,296	0.41	0.24
Tetracycline	18,615	0.90	0.37

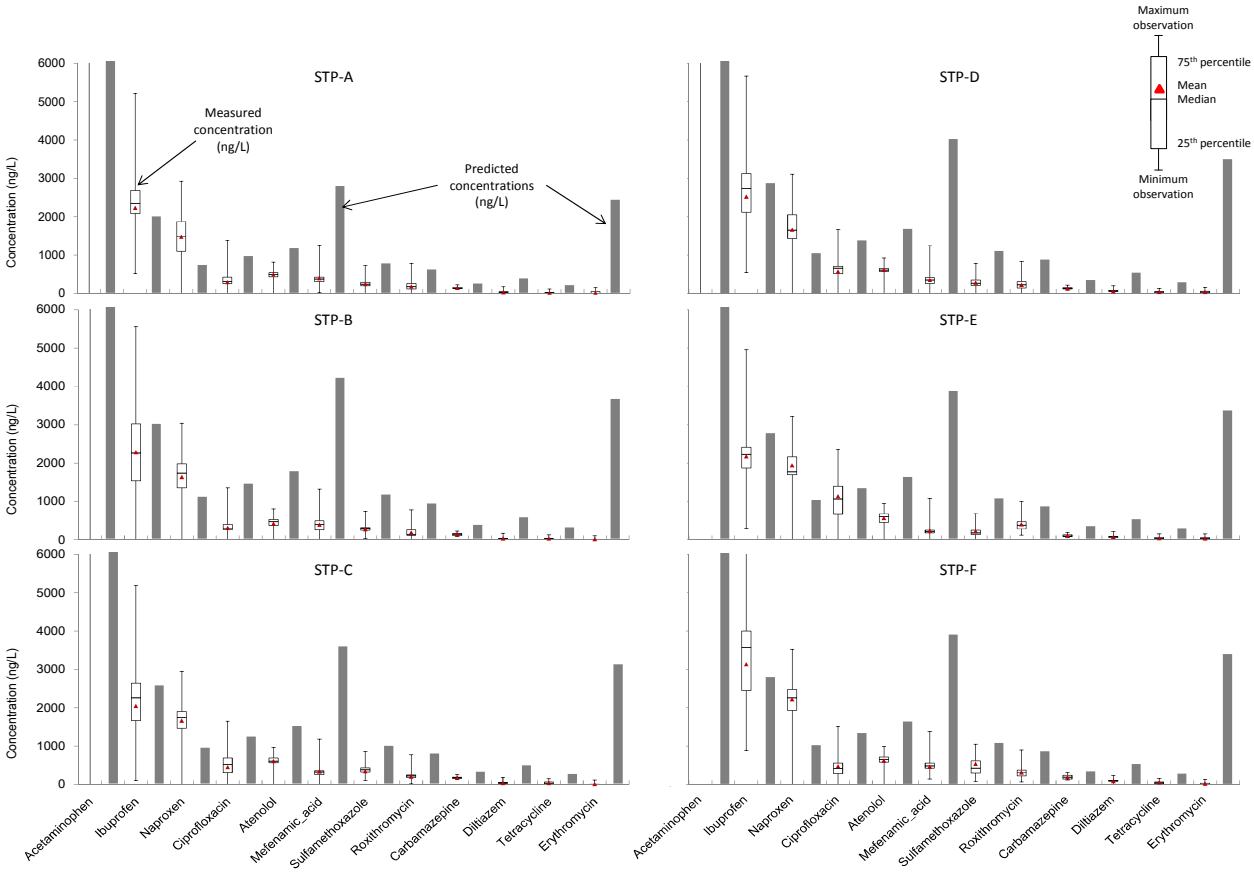


Figure 3.11 Comparison of estimated concentration in use of PPCPs with actual concentration of influents at STP

Concentration estimated with use of medicine mostly turned out to be higher than actually measured concentration. Since measured concentration was found to be lower than estimated concentration, it seems that while moving to the STP, PPCPs have decreased by such mechanisms as photolysis, biodegradation and hydrolysis. Or the used PPCPs may not flow in the STP (Boxall et al., 2012). Looking at the result of biodegradation rate (Table 6.8 in Chapter VI), it is possible that ibuprofen and mefenamic acid have been biodegraded.

3.3.4 Seasonal characteristics of loadings of PPCPs and estrogens

The PPCPs and estrogens detected in the influents of all the STPs in the research area were compared separately in high temperature season [May (n=2) to October (n=3)] and low temperature season [November (n=3) to March (n=3)], and the results are shown in Figure 3.12. From all samples in our analysis but LOQ and LOD, we investigated their characteristics. Ciprofloxacin, levofloxacin, mefenamicacid and bezafibrate show high loadings regardless of water temperature. Norfloxacin and sulfadimidine, which are antibiotics, estrone, and DEET, which is insect repellents, were detected in high loadings in high temperature season. Acetaminophen, ibuprofen, naproxen, fenoprofen and sulfapyridine, which are NSAIDs,

clarithromycin, erythromycin, levofloxacin and tetracycline, which are antibiotic, were detected in high loadings in low temperature season. However, most of the PPCPs detected in the STPs in Korea showed similar loadings regardless of temperature. Estrone was detected in a larger amount in high temperature season than in low temperature season because part of conjugated estrogens is converted into estrone (E1) and 17β -estradiol (E2) (Ashok K. et al., 2013; Vimal K. et al., 2012).

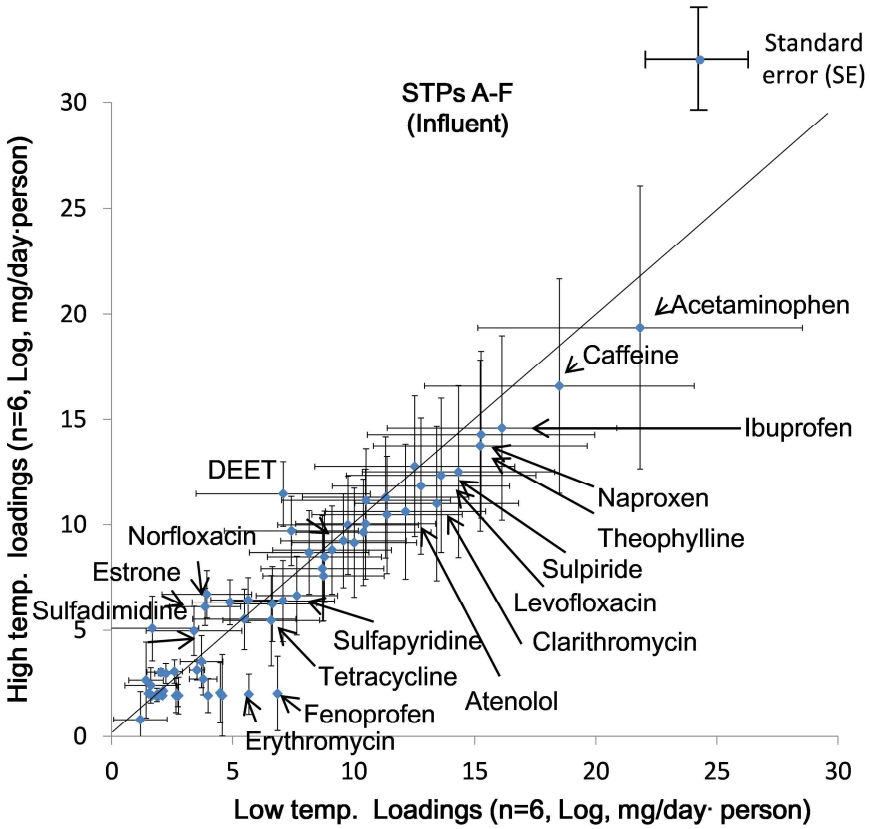


Figure 3.12 The PPCPs and estrogens detected in the influents of all the STPs in the research area were compared separately in high temperature season (May to October) and low temperature season (November to March)

Figure 3.13 shows the differences by concentration under the same condition as Figure 3.12. Though without big difference of PPCPs and estrogens detected from influents by temperature, DEET and estrone showed a little higher concentration at high temperature season while sulfapyridine and sulfadimidine showed a little higher concentration at low temperature season.

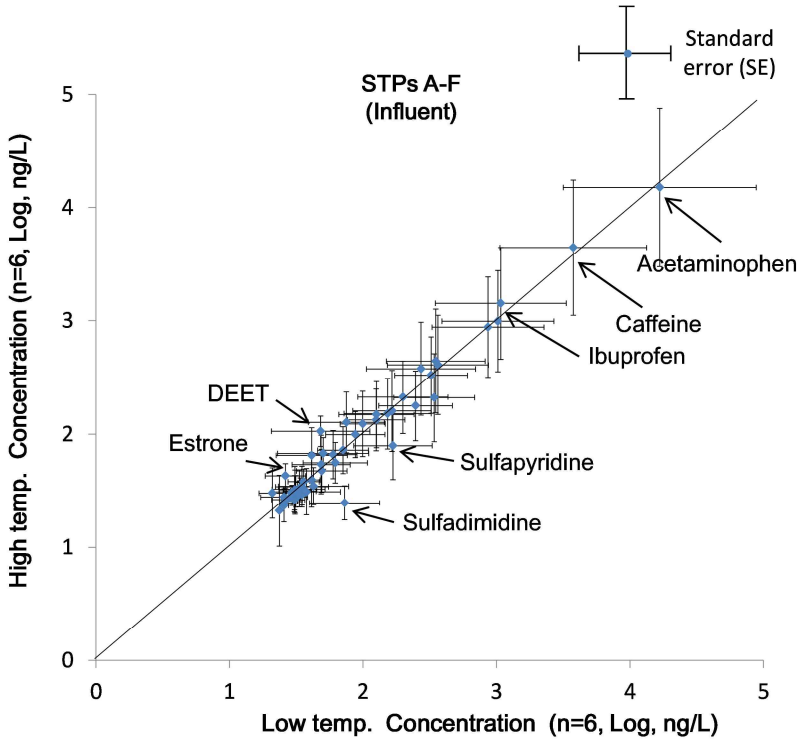


Figure 3.13 Concentration of PPCPs and estrogens detected in the influents of all the STPs in the research area were compared separately in high temperature season (May to October) and low temperature season (November to March)

The next, Figure 3.14 shows the characteristics of PPCPs and estrogens in high temperature season and low temperature season for effluent of representative STPs located at the site of study. Considering the difference of effluents in loadings by season and treatment process, we compared each of STPs by temperature.

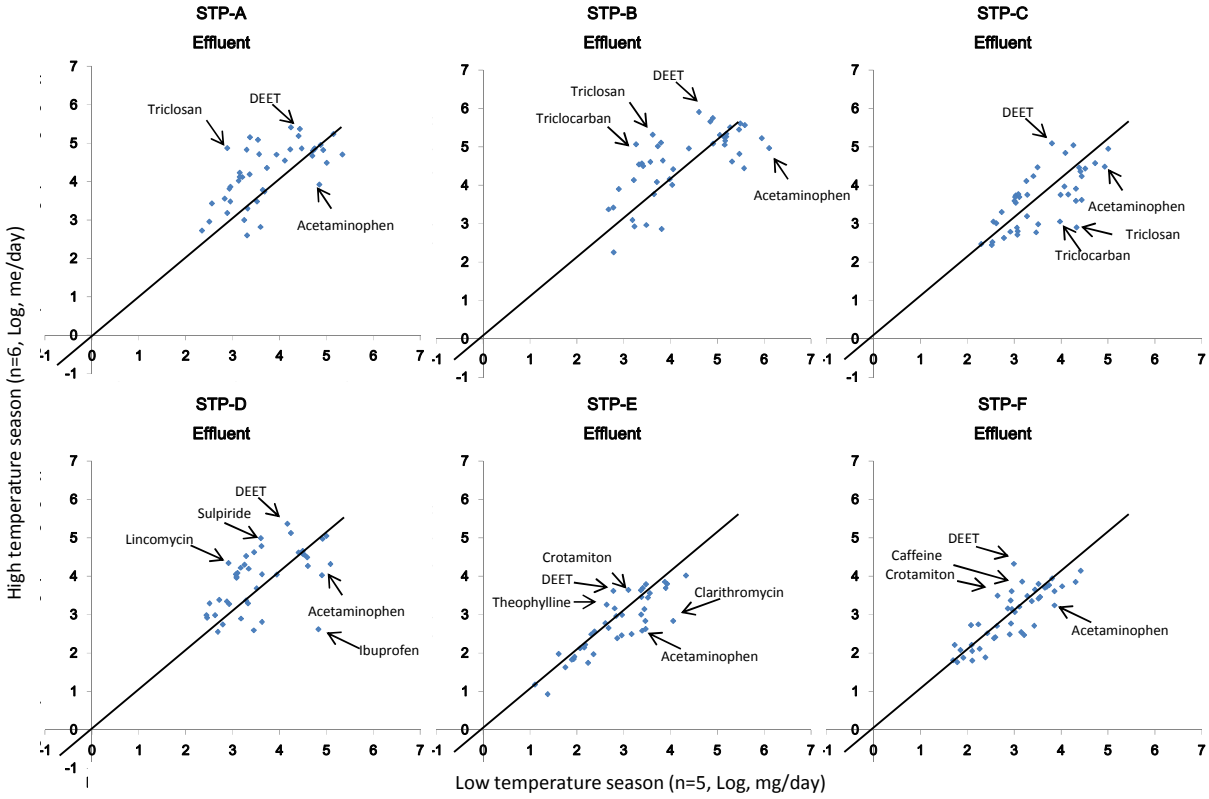


Figure 3.14 Characteristics of PPCPs and estrogens detected in high temperature season and low temperature season from effluent of STPs E and F

For most STPs, acetaminophen showed a high loading at low temperatures season. For STP-D, ibuprofen showed a high loading at low temperatures season. At high temperatures season, DEET and triclosan showed high loadings for most STPs, and besides, there were STPs for which crotamiton and triclocarban showed high loadings. Unlike other STPs, STP-C characteristically showed high loadings of triclosan and triclocarban at low temperatures season.

3.3.5 Effect of SRT on PPCPs and estrogens removal

The Solids Retention Time (SRT) is the average time the activated-sludge solids are in the system. The SRT is an important design and operating parameter for the activated-sludge process and is usually expressed in days. Concretely, the SRT determines the mean residence time of microorganisms inside the reactor. Consequently, only organisms which are able to reproduce themselves during this time can be retained and enriched in the system. According to this definition, high SRTs allow the enrichment of slowly growing bacteria and consequently, the establishment of a more diverse biocenosis with broader physiological capabilities. The longer is the SRT, the longer will be the reaction time and growth of the slowly growing micro-organism and hence longer is the time available for the biodegradation. For several PPCPs a positive effect on their removal has been observed when working at higher SRTs and a critical value for this parameter of 10 day was identified (Clara et al., 2005a, Marius et al., 2011). The calculated removal efficiency

(%) and the measured effluent concentrations (ng L^{-1}) of the different treatment systems in relation to the SRT are shown in Figure 3.15. For target substances, we selected six SRT-related ones reported from the existing studies for verification indicating the target of the STP with the process of MLE and B3 process, which are the treatment plants for examining SRT.

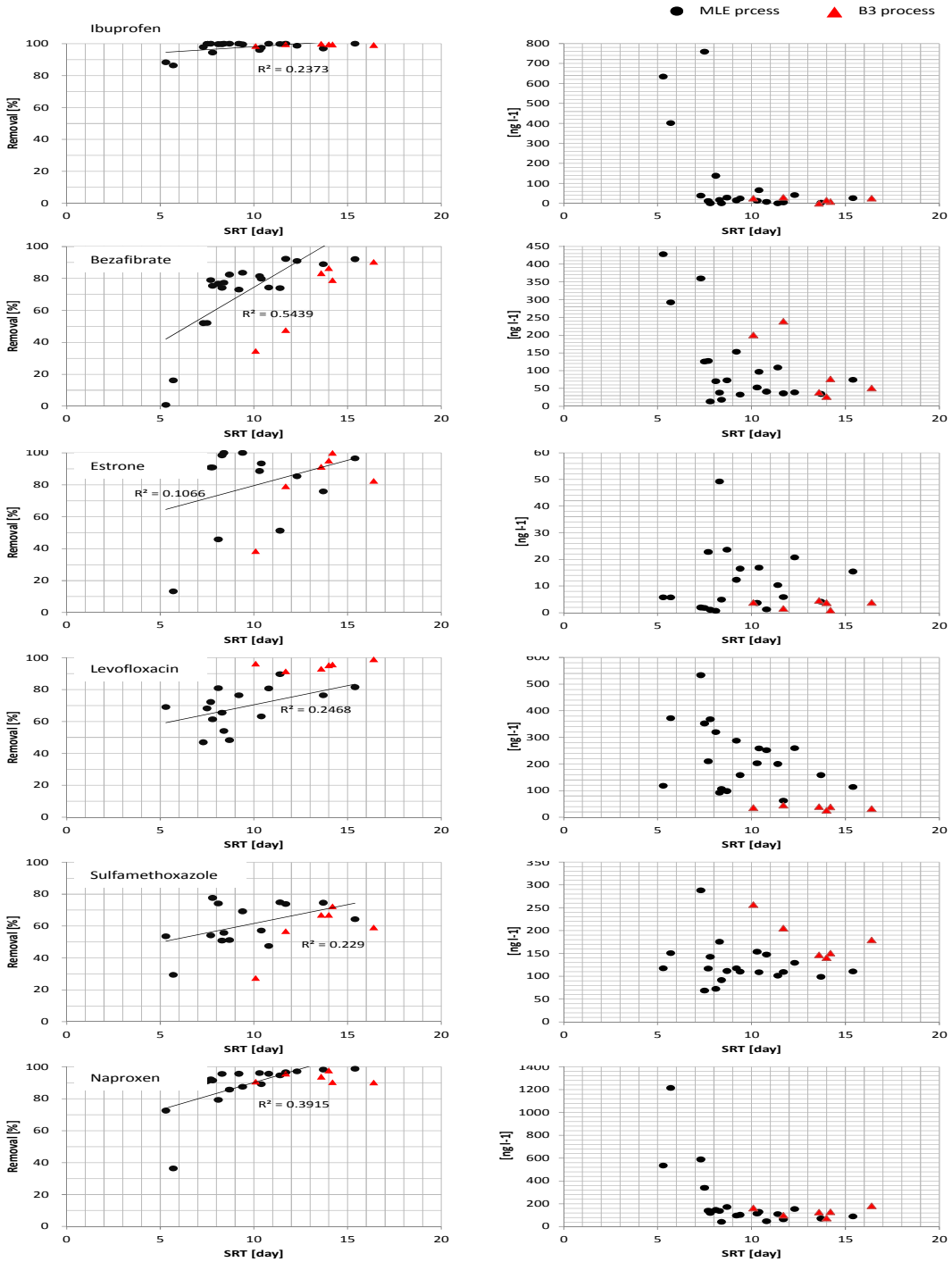


Figure 3.15 Calculated removal efficiencies (%) and measured effluent concentrations (ng L^{-1}) in the wastewater treatment plants

Though Clara et al., (2005a) reported a high removal of ibuprofen when SRT is 10 days and over, our study area showed a removal of over 90% for an SRT of 7 days and over. It shows that operating SRT for over 7 days will increase the removal of ibuprofen at STPs of our study area. Besides while Clara et al., (2005a) reported an effective removal of estrone for over 10 days of STR, at our study area, while for MLE process removal increased with over 7 days of SRT, for B3 process removal was found to be low at around 40%. Also for diclofenac, despite a removal of over 40% reported (Clara et al., 2005a, Marius et al., 2011) with 10 days of SRT, most is flowing in the river without being removed at all STPs of our study area. For bezafibrate, there was a tendency of agreement with Clara's report, so at our study area a high removal is possible with an SRT for over 8 days. Removal efficiency was found to increase with over 8 days of SRT for estrone and levofloxacin, with over 9 days for naproxen. Though the reported article (Clara et al., 2005a, Marius et al., 2011) showed no big difference from the case of our study area, there was a little difference found in temperature and influent water. It is considered that for STPs at our study area, operating with an SRT for over 7 or 10 days will be effective in removing substances appearing in Figure 3.15.

3.3.6 Comparison of removal by primary treatment and biological treatment

The comparative removal efficiency by biological treatment of PPCPs and estrogens flowing into Korean STPs, which use MLE, A2O, B3, and CAS processes, are shown in Figure 3.16. For removal efficiency, we used the mean value of data from two years' research with calculation excluding LOQ and LOD. Removal efficiency shown in Figure 3.16 is the value of calculating PPCPs and estrogens removed until the influent of wastewater and the finish of secondary treatment. Because of not sampling from the water of primary treatment, it was impossible to know how much was removed at the primary treatment. Besides, substances not detected were excluded from the graph while it was impossible to consider SRT and HRT for every STP. So at CAS and other processes, removal efficiency of PPCPs and estrogens were compared and evaluated. Carbamazepine, caffeine and diclofenac are a matter reported to be a low removal in CAS measuring instrument solution (T. Alvarino et al., 2014). While carbamazepine and diclofenac showed a low disposal for all STPs, caffeine showed a removal over 50 % at A2O and B3 processes but a removal of 21.8 % at CAS. The substances that were more efficiently removed by the B3 process than by the CAS process were atenolol, salbutamol, norfloxacin, levofloxacin and diltiazem. The respective removal rates were: atenolol 84.2 %, salbutamol 87.9 %, norfloxacin 92.9 %, levofloxacin 90.8 % and diltiazem 54.8 % in the B3 process; and atenolol 17.1 %, salbutamol 53.2 %, norfloxacin 56.7 %, levofloxacin 50.2 % and diltiazem 2.4 % in the CAS process. The substances that were more efficiently removed by the A2O process than by the CAS prcoess were erythromycin (71.2, 15.3 %), clofibric acid (47.8, 21.8 %) and lincomycin (58.4, 44.4 %). Substances showing a high removal in MLE method than CAS included triclocarban. In the STP F (B3 process), where livestock wastewater is treated, tiamulin, sufathiazole, and lincomycin, which are mainly used on animals, showed low removal rates.

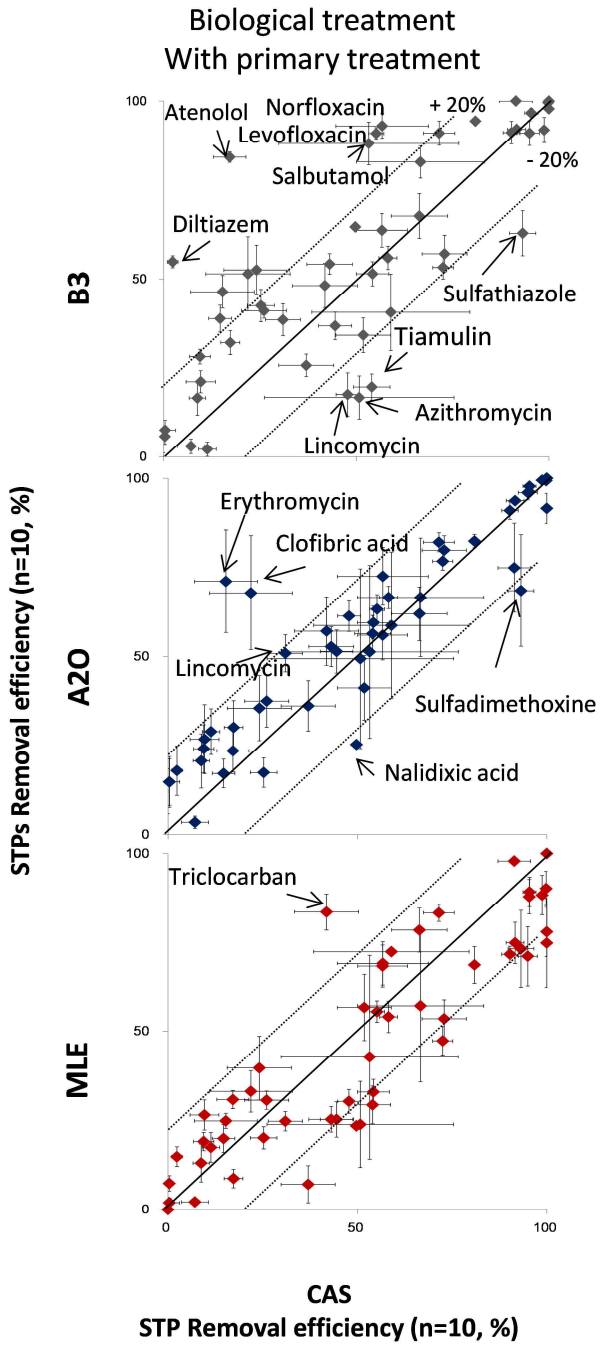


Figure 3.16 The comparative removal rates by biological treatment of PPCPs and estrogens flowing into Korean STPs, which use the MLE, A2O, B3, and CAS processes

3.3.7 Comparison of removal by disinfection processes

The main disinfection used in the STPs in the research areas are chlorination, sodium hypochlorite, ozone and UV treatments. In order to confirm the efficiency of each chemical treatment for removal of PPCPs and estrogens, the removal efficiencies of ozone, UV, chlorination,

and sodium hypochlorite were compared (Figure 3.17). Result of the analysis was interpreted in the same method as 3.3.6. So by the standard of chlorination, characteristics of PPCPs and estrogens being removed at other disinfection processes were compared. Regarding disinfection by ozone and UV, the removal of PPCPs appeared to be slightly more effective by UV disinfection, but the removal efficiency of each PPCP varied. Ketoprofen, ibuprofen, and triclosan showed removal rates of 75.7 %, 85.6 %, and 80.8 %, respectively, in UV disinfection, and 7.2 %, 27.7 %, and 10.5 %, respectively, in chlorination disinfection. Griseofulvin was removed by 15.2 % in UV disinfection and 50.1 % in ozone disinfection; and norfloxacin was removed by 30.6 % in UV disinfection and 68.7 % in ozone disinfection. Sulfadimethoxine was removed by 33.7 % in UV disinfection and by nearly 100 % by ozone disinfection. 2QCA, ciprofloxacin, caffeine, and DEET are reported to be a mater in low treatment efficiency with ozone. In the present study, however, 2QCA was hardly treated with Sodium hypochlorite but showed a removal of around 40 % with ozone. Ciprofloxacin, caffeine, and DEET showed low treatment efficiency at all disinfection process (Basile T. et al., 2011). There have been many studies on the removal of PPCPs by ozone disinfection, and its efficiency is highly rated (Westerhoff et al., 2005; Ternes et al., 2002; Vongna et al., 2004). Since ozone treatment at STP is for the purpose of disinfection, removal of PPCPs and estrogens showed lower efficiency than the existing reports. (Ilho Kim et al., 2009). STP-E is carrying out UV disinfection using UV 254 nm (UV intensity 0.025mW/cm^2). According to studies on the treatment of PPCPs using UV, diclofenac, ketoprofen isopropylantipyrine, sulfamethoxazole, diliazem, dipryridamole and clofibric acid showed a high removal efficiency of over 90 %. At STP-E however, there were no PPCPs with a removal efficiency of over 90 % found. In Ilho Kim's study, experiment proceeded with UV_{41w} lamp and UV intensity of 0.639 mW/cm^2 was over 10 times higher than STP-E. Thus, for STP-E, it was impossible to observe such removal efficiency as Ilho Kim (Ilho Kim et al., 2009).

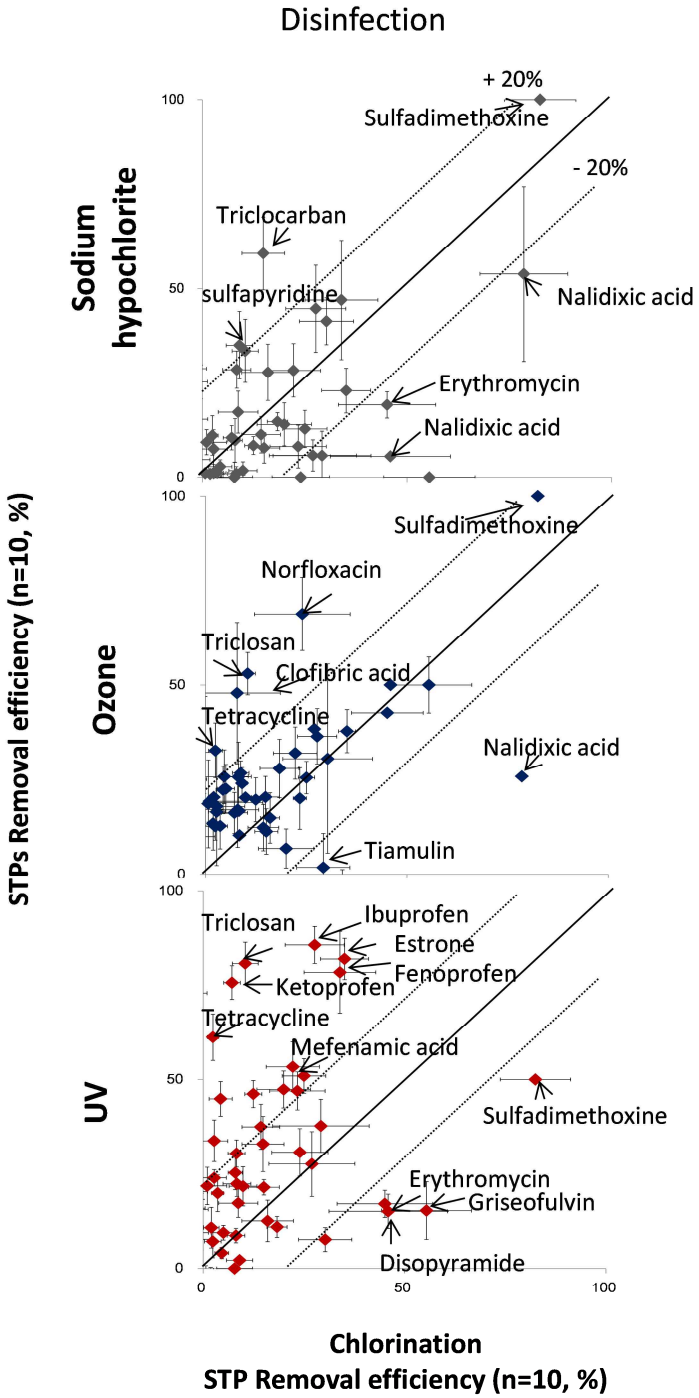


Figure 3.17 Removal efficiency of PPCPs and estrogens by disinfection

3.4 Conclusions

In this study, data from both the composite and spot samplings, which have high correlation, were used.

1) The main PPCPs found in Korean STPs during the research period were acetaminophen, caffeine, ibuprofen, naproxen, theophylline, ciprofloxacin, sulpiride, levofloxacin, DEET, clarithromycin, bezafibrate, atenolol, mefenamic acid, sulfamethoxazole, ketoprofen, and roxithromycin. Regarding the relative amounts of PPCPs, NSAIDs were most prevalent, followed by antibiotics, BLLAs, and estrogens. In the comparison of the STP-F, where livestock wastewater is also treated, and ordinary STPs, the concentrations of triclosan, which is used as an antimicrobial agent in cosmetics, were high in the ordinary STPs, and tiamulin, chlortetracycline, and sulfadimethoxine were detected only in the STP-F.

2) Besides, comparing PPCPs and estrogens remaining in the influent of STP among seasons ciprofloxacin, levofloxacin, mefenamicacid and bezafibrate showed high concentrations regardless of season. Norfloxacin, sulfadimidine, estrone and DEET showed high loading in the high temperature, while acetaminophen, ibuprofen, naproxen, fenoprofen, sulfapyridine, clarithromycin, erythromycin, levofloxacin and tetracycline are high loading in the low temperature.

3) In the comparison of the removal efficiencies of the biological treatments of the STPs, the MLE and A2O processes were found to be more efficient than the CAS process in managing PPCPs effectively. In the case of treating livestock wastewater as well, the A2O process was found to be more efficient than the B3 process. Regarding the disinfection method, chlorination and sodium hypochlorite were found to be inefficient in removing PPCPs; thus, UV and ozone disinfections should be considered to reduce the amount of PPCPs flowing into rivers.

4) In Korea, there are many STPs using CAS method and chlorination. To reduce the contamination of river by PPCPs and estrogens, upgrading the treatment method as well as adding ozone or UV process is a good way for effective management. Because it is expected that the use of PPCPs will increase (KNSO. 2013), STPs play an important role in managing the flow of PPCPs and estrogens into rivers. Besides, for effective control of PPCPs and estrogens, we can put Solids Retention Time (SRT) at over 7-10 days and increase the efficiency in removing bezafibrate, naproxen, estrone and levofloxacin.

Therefore, it is necessary to introduce an effective wastewater treatment method, and it is urgent to establish an expectable model. However, the research on PPCPs and estrogens in Korea is still insufficient, and continued attention and support are required. Results investigated in this chapter will be used as data for estimation model of PPCPs and estrogens appearing at STP in Chapter VII. Besides, characteristics of treating PPCPs and estrogens by diverse biological treatments and disinfection methods will be used as data absolutely needed for effective management of STPs in Chapter VII.

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CHAPTER IV

CHRACTERISTICS OF VETERINARY PHARMACEUTICALS REMOVAL AT SEWAGE TREATMENT PLANTS TREATING BOTH LIVESTOCK WASTEWATER AND DOMESTIC WASTEWATER

4.1 Introduction

Though veterinary pharmaceuticals (VPs) are used for protecting or treating animals from disease, problems of generating resistance to VPs for microbes are reported in many countries in relation to their abuse and misuse (Boxall et al., 2002; Halling-Sørensen et al., 2002). What is at issue here, among others, is VPs used for treating an animal's disease or facilitating its growth (Huang, C.H. et al., 2001). It is because despite the increased productivity, inadvertent use of VPs for livestock ultimately brings them on to remain in our food on the table (Park et al., 2007; Koschorreck et al., 2002; Yang, S. et al., 2004). Excess use of pharmaceuticals generates resistant bacteria making it even harder to treat the disease of livestock (Park et al., 2007). Also, livestock wastewater generated from stockbreeding facilities contains large amounts of VPs. That is why we need to make study on characteristics of VPs removal and whether facilities of processing livestock wastewater are removing them effectively. When VPs and resistant bacteria remaining in the livestock are delivered into human body, it can cause a serious harm by making it harder to treat disease. Besides, VPs remaining after the process of the treatment facilities can flow into a river or steam causing problems to an ecosystem. According to report, wastewater containing pharmaceuticals and personal care products (PPCPs), VPs and estrogens discharged into a river contributes to water pollution of ecosystem and brings on disturbance of ecological equilibrium (Arvanitidou, M. et al., 1996; Carballa, M. et al., 2004; Boxall et al., 2003). Existence of low-concentration residual PPCPs, VPs and estrogens in water environment has two implications: More directly, these compounds have side effects on humans acting as a drinking water source. Secondly, they are very likely to work on aquatic life as potential toxic matter (Yang, S. et al., 2004). Despite efforts to detect such PPCPs, VPs and estrogens, however, we still don't have much knowledge about VPs behavior and residue at natural ecosystem and treatment plants (Arvanitidou, M. et al., 1996). Therefore, we need to inquire into the kinds of VPs mainly detected in Korea and characteristics of the VPs remaining in the wastewater and sludge of sewage treatment plants (STPs). The best way to solve these problems is considered a proper use of PPCPs, VPs and estrogens but this has limitations in practical use. So one practicable methods can be effectively removing and managing PPCPs, VPs and estrogens introduced in the STPs. The present study will grasp the removal characteristics and behavior of residual VPs in the livestock wastewater and

domestic wastewater introduced in the STPs. Grasp VPs chiefly used and detected in Korea accurately. Then, verify whether VPs are being removed from STP and see if there is possibility for VPs remaining in the wastewater sludge ant them being emitted into environment. Finally, verify the behavior at STP of VPs chiefly detected in Korea and their possibility to leak into environment.

4.2 Materials and methods

4.2.1 Usage of VPs in Korea

Among livestock and fishery antibiotics used in Korea (Table 4.1), tetracycline antibiotics account for around 49% of the total usage with around 700 tons a year (MEK. 2008).

Table 4.1 Usage of antibiotics for livestock in Korea (ton/year)

Antibiotic	2002	2005	2007	2009	
				ton	%
Tetracycline	774.3	733.5	723.6	783	49.2
Penicillin	127.7	137.6	169.2	208	13.1
Sulfonamide	208.8	182.6	162.2	212	13.3
Aminoglycoside	74.4	79.8	82.8	72	4.5
Macrolide	59.8	49.6	58.6	65	4.1
Quinolone	40.8	42.7	44.5	53	3.3
Polypeptide	32.1	33.9	31.8	49	3.1
Lincosamide	11.2	10.8	12	14	0.9
Others	250	268	119	137	8.6
Total	1579.1	1538.5	1403.7	1593	100

Among tetracycline group, chlorotetracycline was most used, and followed by oxytetracycline (MEK. 2008). Tetracycline descent was followed by sulfonamide and penicillin in the order, and the sum of these three kinds in upper rank accounts for around 75% of the total usage. Besides, aminoglycoside, macrolide, quinolone and polypeptide are much used in the order, while cepha descent in much use for treating humans is used relatively small for animals (MFDS 2006). Sulphathiazole in sulfonamide antibiotics, amoxicillin and ampicillin in penicillin, neomycin and streptomycin in aminoglycoside, and enrofloxacin in quinolone are much used respectively. (MEK 2008; MFDS 2006)

4.2.2 Collection of livestock night soil

There are many livestock farms on the Gyeongan River basin. Livestock excretions occurring daily from a livestock farms are divided into feces and urination as show in Figure 4.1. Feces filtered out are moved to a fertilizer plant to be used as its manure. Fertilizer plant, which is not located at the Gyeongan River basin, is not likely to contaminate Gyeongan River in the course of producing fertilizer. Urine is collected and moved by car to a STP to be processed together with domestic wastewater. On Gyeongan River operating the livestock farms because apply such a

system, it is likely that the nonpoint source influent to the river is thought relatively low. According to data reported in 2012, the number of heads of cattle where waste was treated in STP-F was 98,576, consisted of pigs, cows and hens (KNSO. 2013).

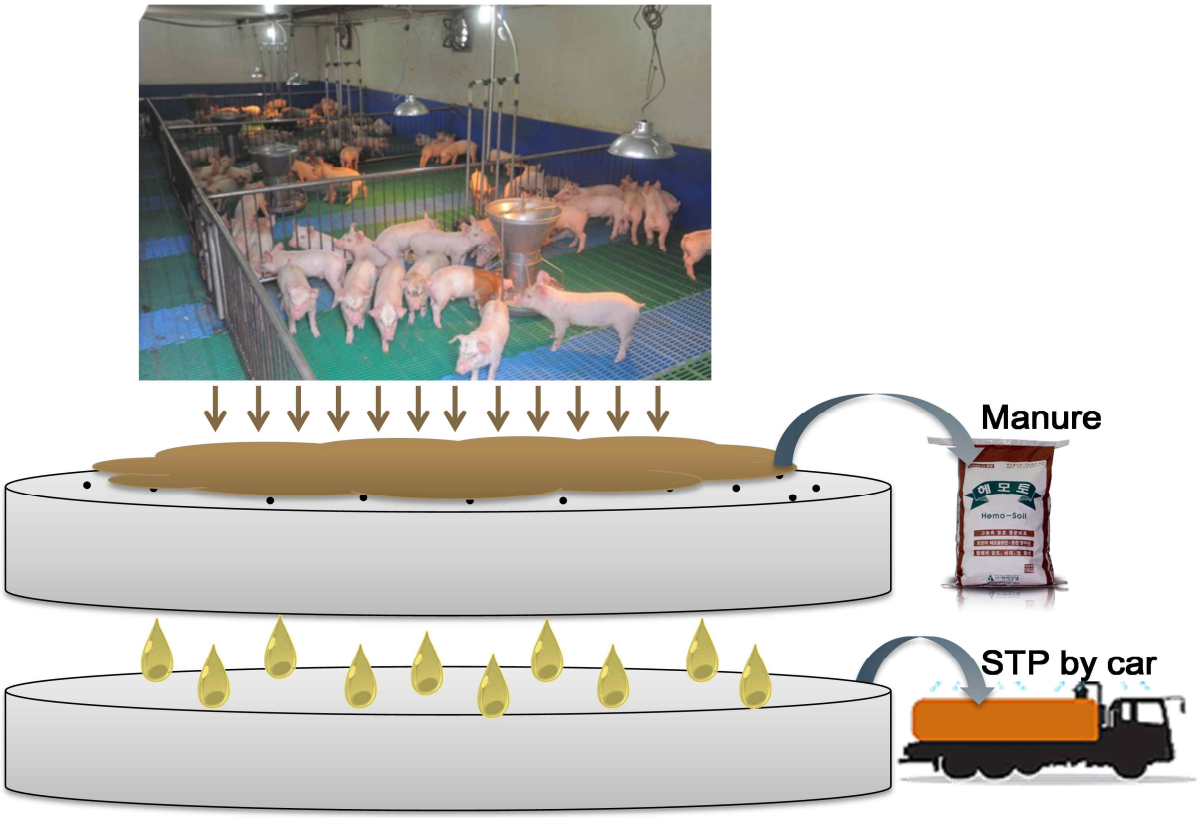

Figure 4.1 Diagram for treating livestock farm located at Gyeongan River

4.2.3 STP surveyed and sampling points

The target STP-F is a facility to treat livestock wastewater and then process it in connection to wastewater. And it operation capacity is 48,000 m^3/day, but actual treatment volume was 40,573 m^3/day (2013 average), and livestock wastewater process volume of 308 m^3/day (2013 average). STP-F, as shown in Figure 4.1, treats together livestock wastewater and human excretions in septic tank collected with vehicle. Livestock wastewater and human excretions are being processed by HBR-II (Hanmee Bioreactor Process-II). HBR-II process keeps the entire process odorless, stabilizes sludge and maintains at increased dehydration efficiency installing an extra anaerobic tank on the fore-end part of reactor, which is used for intermittent aeration reactor to remove both nitrogen and phosphorus. The processed livestock wastewater flows into the STP to go through Bio Best Bacillus (B3) process with wastewater. B3 process is an advanced treatment technology to remove wastewater, organic matters of livestock excretions, nitrogen and phosphorus by culturing

bacillus germs in B3 reactor using its nature of sporation. Figure 4.2 shows the entire process of the STP and sampling points.

Excretions collected by a car (c) and stock wastewater (d) are kept in a storage tank for 3 to 4 days and then receive organic matter removal and height treatment for about 8 hours in HBR-II method. Finally treated livestock excretion wastewater passing through a settling pond is mixed with domestic wastewater and chlorinated and then discharged through the process of (a) grit chamber, primary settling tank, B3 process, sedimentation tank and microdisk filtration. Sampling was carried out at 10 points in all with a total four times of solid sampling from May 2013 through January 2014. For effluent, secondary effluent and influent of the STP, sampling was conducted a total of eleven times from 2011 through January 2014.

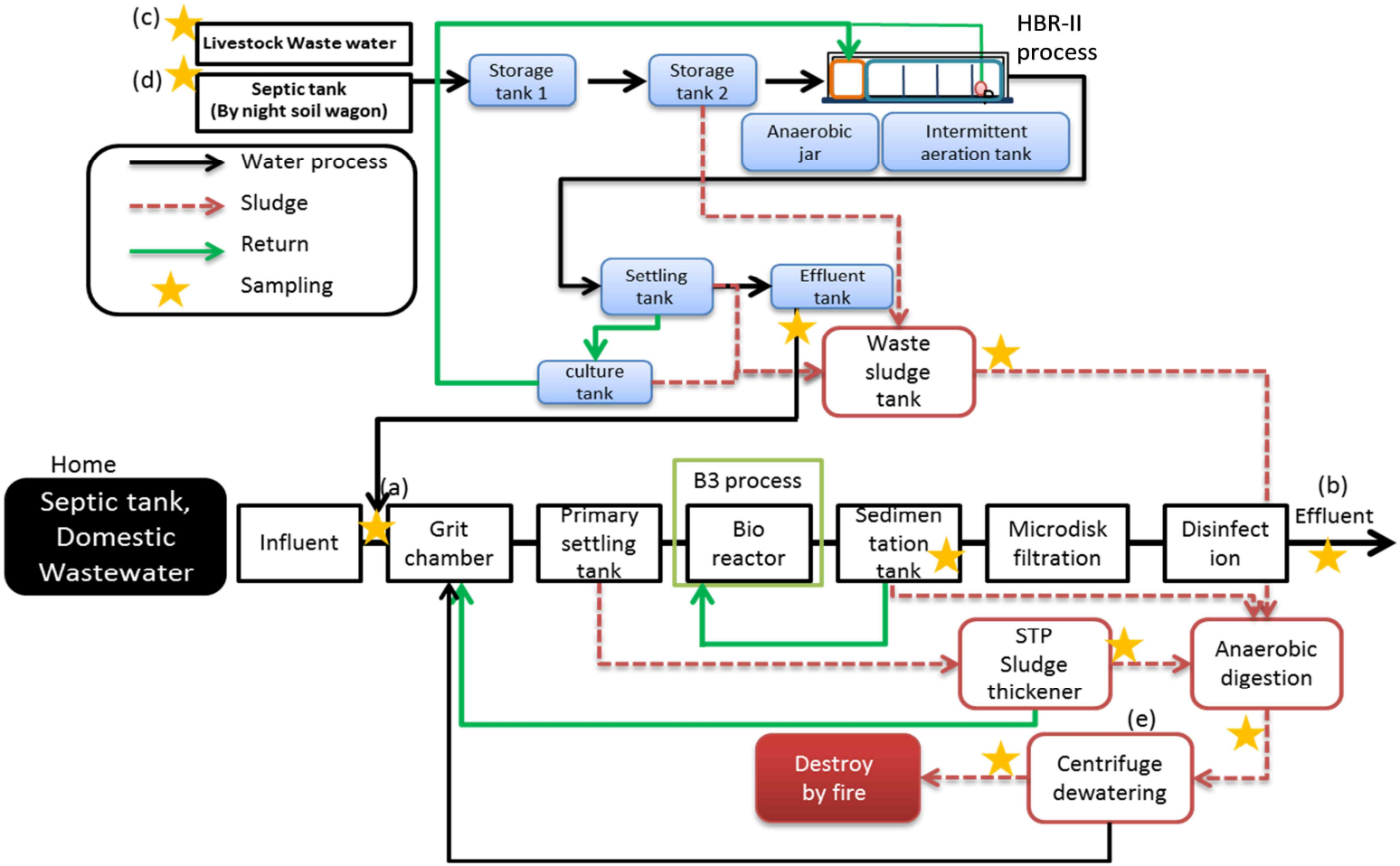

Figure 4.2 Treating process diagram for STP that treats livestock wastewater and wastewater

4.2.4 Extraction of solid sample

1g of L^{-1} ascorbic acid was added to 500 mL or 1000 mL quantity of samples taken. Samples including solid were put to centrifugation for 10 minutes with 3000 rpm to separate liquid from solid to learn about residual PPCPs and estrogens in solids. The same method (Chapter III) was used for liquid in PPCPs and estrogens. From each of separated solids, 1 g–wet was used for extraction to inject 50 uL into the surrogate of each. First, prepare PPCPs by adding methanol in the ratio of 9:1 (v/v) to the reagents of (A) pH 2 by HCl (B) pH 7 and (C) pH 11 by NaOH. Then put 10mL of reagent (B) in 1 g sample and erupt it for 10 minutes in ultrasonication 40 ℃. Then, conduct centrifugation for 10 minutes with 2500 rpm and take the supernatant. In the same method, conduct two times with reagent (B), one time with (A), and two times with (C) to finish eruption. For eruption of estrogens, add 10 mL of MeOH : Acetone (50: 50, v/v) to 1 g-wet of sample and conduct centrifugation of ultrasonication two times in the same condition as PPCPs eruption. Then, carry out centrifugation on MeOH : Pure water (50: 50, v/v) two times in the same method. The erupted PPCPs and Estrogens samples will go through pretreatment and analysis in the same process as liquid experiment (Narumiya M. et al., 2013). This chapter analyzed the solid sample from points (c), (d) and (e) as shown in Figure 4.2, putting the recovery rate of each sample on Table 4.2.

Table 4.2 Recovery rate of point (c) Livestock wastewater, (d) Septic tank and (e) dewatering sludge

		Recover rate (%)											
		Jul-13			Sep-13			Dec-13			Jan-14		
No.	Compounds	(c) livestock	(e) septic tank	(e) sludge	(c) livestock	(e) septic tank	(e) sludge	(c) livestock	(e) septic tank	(e) sludge	(c) livestock	(e) septic tank	(e) sludge
1	Acetaminophen	40%	31%	36%	33%	43%	33%	44%	38%	38%	34%	38%	32%
2	Antipyrine	94%	79%	94%	80%	69%	76%	81%	90%	96%	91%	92%	99%
3	Atenolol	8%	11%	6%	51%	92%	97%	85%	72%	65%	60%	60%	47%
4	Azithromycin	50%	39%	46%	48%	33%	28%	30%	27%	25%	32%	44%	44%
5	Bezafibrate	78%	68%	71%	114%	135%	131%	51%	117%	107%	77%	69%	70%
6	Caffeine	56%	51%	62%	68%	70%	77%	59%	77%	70%	78%	47%	53%
7	Carbamazepine	39%	35%	72%	72%	37%	46%	33%	57%	75%	54%	29%	58%
8	Ceftiofur	-	-	-	-	-	-	-	-	-	-	-	-
9	Ciprofloxacin	31%	37%	36%	39%	36%	24%	33%	22%	12%	37%	23%	13%
10	Clarithromycin	64%	64%	77%	58%	55%	42%	58%	20%	34%	5%	53%	57%
11	Clenbuterol	76%	68%	70%	69%	78%	81%	91%	50%	75%	26%	85%	90%
12	Clofibric_acid	47%	33%	75%	54%	46%	37%	30%	53%	71%	54%	31%	69%
13	Crotamiton	55%	51%	54%	47%	40%	41%	41%	33%	49%	47%	33%	50%
14	DEET	36%	55%	64%	55%	48%	54%	51%	40%	58%	65%	47%	56%
15	Diclofenac	56%	49%	56%	60%	46%	34%	44%	36%	47%	35%	33%	45%
16	Diltiazem	57%	60%	68%	34%	55%	42%	56%	20%	35%	54%	64%	57%
17	Dipyridamole	37%	39%	26%	45%	37%	27%	34%	23%	20%	54%	64%	54%
18	Disopyramide	53%	47%	62%	33%	35%	28%	53%	14%	26%	43%	54%	46%
19	Enrofloxacin	33%	27%	36%	29%	36%	14%	23%	52%	22%	31%	33%	4%
20	Erythromycin	41%	33%	42%	37%	20%	19%	38%	21%	29%	9%	44%	35%
21	Ethenzamide	-	-	-	-	-	-	-	-	-	-	-	-
22	Fenoprofen	42%	35%	89%	89%	42%	64%	33%	64%	96%	57%	35%	104%
23	Furosemide	51%	38%	63%	47%	38%	45%	35%	67%	57%	56%	43%	42%
24	Griseofulvin	42%	35%	89%	89%	42%	64%	33%	64%	96%	57%	35%	104%
25	Ibuprofen	43%	35%	67%	44%	21%	3%	37%	30%	58%	38%	27%	49%
26	Ifenprodil	56%	60%	68%	34%	35%	42%	56%	30%	35%	54%	64%	57%
27	Indometacin	25%	35%	44%	15%	29%	36%	34%	64%	53%	16%	28%	62%
28	Isopropylantipyrine	94%	79%	94%	79%	68%	75%	81%	90%	96%	91%	92%	99%
29	Ketoprofen	42%	35%	89%	89%	42%	64%	33%	64%	96%	57%	35%	104%
30	Levofloxacin	31%	34%	29%	27%	29%	34%	44%	6%	4%	1%	26%	7%
31	Lincomycin	-	-	-	-	-	-	-	-	-	-	-	-
32	Mefenamic_acid	36%	59%	41%	43%	77%	49%	38%	38%	42%	4%	38%	30%
33	Metoprolol	77%	78%	83%	86%	72%	85%	83%	71%	84%	52%	90%	97%
34	Nalidixic_acid	39%	35%	72%	72%	37%	46%	33%	57%	75%	54%	29%	58%
35	Naproxen	41%	34%	88%	89%	42%	64%	38%	64%	96%	57%	35%	104%
36	Norfloxacin	41%	26%	35%	47%	36%	29%	38%	42%	31%	34%	21%	31%
37	Oxytetracycline	24%	23%	21%	39%	31%	25%	35%	41%	21%	31%	11%	35%
38	Pirenzepine	56%	50%	61%	68%	70%	77%	59%	77%	70%	78%	47%	53%
39	Primidone	45%	35%	40%	57%	53%	54%	40%	59%	52%	54%	46%	54%
40	Propranolol	53%	47%	62%	33%	35%	28%	53%	14%	26%	43%	54%	46%
41	2-QCA	21%	23%	32%	21%	14%	16%	16%	13%	11%	11%	24%	31%
42	Roxithromycin	94%	88%	87%	69%	55%	57%	89%	26%	39%	26%	80%	85%
43	Salbutamol	62%	75%	54%	113%	91%	102%	39%	49%	53%	51%	27%	38%
44	Sulfadimethoxine	24%	24%	45%	58%	33%	41%	30%	41%	51%	34%	29%	43%
45	Sulfadimidine	57%	51%	67%	94%	62%	73%	57%	72%	84%	58%	48%	67%
46	Sulfamerazine	53%	43%	61%	91%	64%	75%	51%	70%	76%	61%	43%	66%
47	Sulfamethoxazole	71%	61%	75%	64%	72%	72%	62%	78%	84%	66%	54%	81%
48	Sulfamonomethoxine	53%	43%	60%	90%	64%	74%	51%	70%	76%	61%	43%	66%
49	Sulfapyridine	49%	43%	58%	79%	51%	61%	45%	61%	69%	48%	38%	58%
50	Sulfathiazole	40%	30%	54%	70%	49%	58%	21%	55%	61%	46%	25%	34%
51	Sulpiride	-	-	-	-	-	-	-	-	-	-	-	-
52	Tetracycline	44%	43%	31%	39%	41%	35%	35%	41%	31%	44%	31%	47%
53	Theophylline	40%	27%	57%	46%	36%	40%	50%	83%	82%	77%	38%	61%
54	Thiamphenicol	39%	30%	53%	70%	49%	58%	21%	55%	61%	46%	25%	34%
55	Tiamulin	56%	60%	68%	14%	25%	32%	56%	20%	35%	24%	64%	57%
56	Triclosan	36%	35%	38%	24%	35%	2%	45%	26%	21%	33%	34%	25%
57	Trimethoprim	56%	51%	62%	68%	70%	77%	59%	77%	70%	78%	47%	53%
58	Tylosin	56%	60%	68%	14%	15%	22%	56%	20%	35%	4%	64%	57%
59	Chlortetracycline	24%	23%	21%	49%	31%	15%	35%	49%	58%	51%	27%	46%
60	Triclocarban	36%	34%	36%	42%	31%	40%	40%	26%	30%	43%	29%	31%
61	Erythromycin-HO	61%	63%	77%	52%	41%	32%	83%	33%	45%	12%	72%	52%

4.2.5 Calculations

In most cases, removal efficiency is calculated by concentrations of inflow into the STP and discharge after treatment as Equation 1.

$$\text{Removal efficiency}\ (\%) = \frac{\text{STP}_{\text{in}} - \text{STP}_{\text{out}}}{\text{STP}_{\text{in}}} \times 100$$

eq1

where STP_{in} is concentration of PPCPs and estrogens in influent of STP, STP_{out} is concentration of PPCPs and estrogens in final effluent of STP.

The mass load of target compounds that was lost in STP due to the sum of all transformation processes (STP_{Lost}) was calculated according to Equation 2 (A. Ziylan et al., 2011; A.S. Stasinakis et al., 2010)

$$\text{STP}_{\text{Lost}} = (\text{Q}_{\text{in}} \times \text{C}_{\text{in}} + \text{Q}_{\text{L.in}} \times \text{C}_{\text{L.in}} + \text{Q}_{S.\text{in}} \times \text{C}_{S.\text{in}}) - (\text{Q}_{out} \times \text{C}_{out}) - (\text{M}_{\text{dew .sludge}} \times \text{C}_{\text{dew .sludge}})$$

eq2

※ $M_{dew.sludge}$: Mass of dewatered sludge, $C_{dew.sludge}$: Compounds concentration

※ L : Livestock, S : Septic tank

where Q_{in} and Q_{out} are the flow rates of influent(a) and effluent(b), respectively (m^3 for day), C_{in} and C_{out} the total concentrations of the PPCPs and estrogens in influent(a) and effluent(b), respectively (mg m^{-3}), $Q_{L.in}$ are flow rate of livestock influent(c) (m^3 for day), $C_{L.in}$ the total concentrations of the PPCPs and estrogens in livestock influent(c) (mg m^{-3}), $Q_{S.in}$ are flow rate of septic tank(d) (m^3 for day), $C_{S.in}$ the concentrations of the PPCPs and estrogens in septic tank(d), $M_{dew.sludge}$ the mass of dewatered sludge(e), $C_{dew.sludge}$ the PPCPs and estrogens concentration in dewatered sludge(e) and STP_{Lost} the mass of target compounds that was lost during treatment (mg d^{-1}). Using the following formula, we are able to know the actual removal efficiency at STPs and manage the residual PPCPs and estrogens on sludge.

4.3 Results and discussion

4.3.1 Occurrence of VPs in STP

While diverse VPs are used for livestock, its excretions and livestock wastewater are flowing into the STPs (Park et al., 2007). For livestock wastewater, this study used the result of measurements in four times from 2013 through 2014.

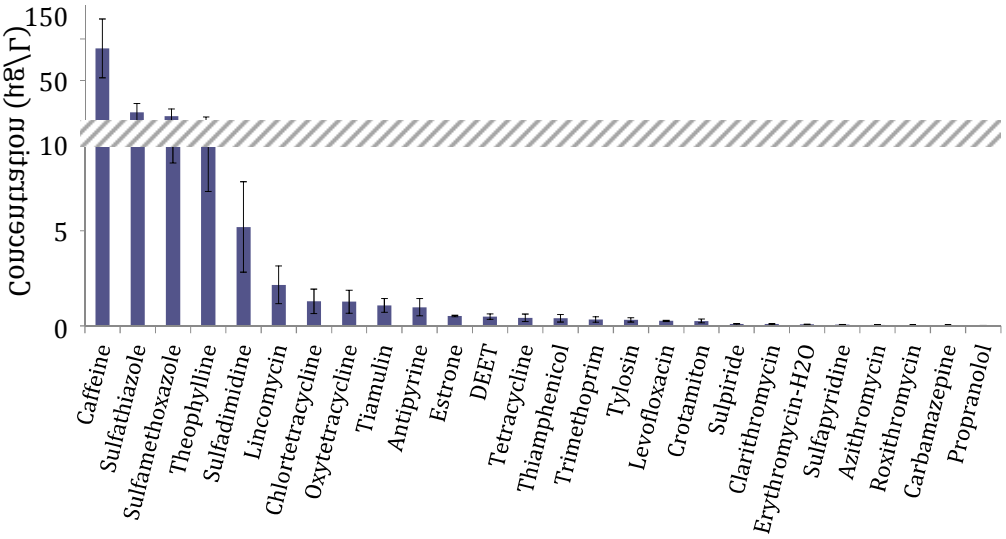

Figure 4.3 Concentration of livestock wastewater (STP F)
(During the study period, our subject was limited to the substances detected from the influents of the STP F, except LOQ and LOD)

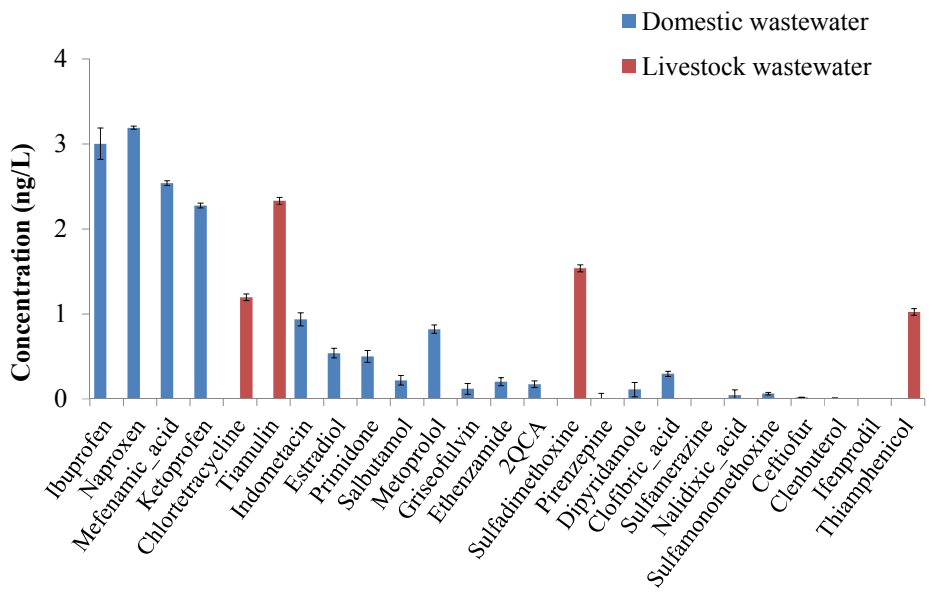

Figure 4.4 Substances detected from influent of STPs in domestic wastewater or livestock wastewater
(The following indicated the mean concentration and standard error for the same period as Figure 4.3.)

From wastewater appeared atenolol used for treating hypertension, triclosan used for cosmetics antimicrobial, acetaminophen which is anodyne antipyretic pharmaceutical (Santos et al., 2010),

In livestock wastewater influents into the Gyeongan River, various VPs have been detected. Caffeine was detected at the highest concentration, which was followed by sulfathiazole and sulfamethoxazole. The reason for the high caffeine concentration is the use of trees containing caffeine as ingredients of livestock feed in South Korea. Residual antibiotics, such as sulfathiazole, sulfamethoxazole, and tetracyclines, were also detected at relatively high concentrations. The veterinary pharmaceuticals that were detected in the STP were pretreated with HBR processing before they were mixed with general wastewater and treated with B3 processing.

Among detected PPCPs, those only from livestock wastewater include tiamulin, sulfadimethoxine, chlortetracycline, thiamphenicol. These substances are all reported as pharmaceuticals used for animals. It was possible to distinguish VPs among pharmaceuticals used in Korea by using pharmaceuticals detected from livestock wastewater and domestic wastewater.

Pharmaceuticals considered to be used by both humans and animals included enrofloxacin, estrone, oxytetracycline, tylosin, sulfadimidine. The reason for a high concentration of caffeine in livestock wastewater is that plants containing caffeine are used for stock feed. Besides, substances such as naproxen, ibuprofen, mefenamic acid, diclofenac and triclosan on the vertical axis are those only detected from domestic wastewater, and were never detected from stock wastewater.

4.3.2 Loading of PPCPs and estrogens in dewatering sludge

PPCPs and estrogens on the dewatering sludge at STPs were erupted for analysis. Figure 4.5 shows day production of PPCPs and estrogens remaining in the sludge. From left to the right of the graph shows the substances with more residues in the sludge. 51 kinds of PPCPs were detected from dewatering sludge in a large quantity of levofloxacin, tiamulin, sulpiride. Tiamulin, chlortetracycline, sulfadimethoxine and thiamphenicol detected only from livestock wastewater were also detected from dewatering sludge, with a large amount of tiamulin among them. Diverse PPCPs are adsorbed onto dewatering sludge and leaked out to the environment (Aleksandra Jelic et al., 2011). Considering that sludge containing PPCPs and estrogens can be effluent to environment anytime, it requires both care about this fact and studies on the reduction and efflux of PPCPs and estrogens in the process of reuse.

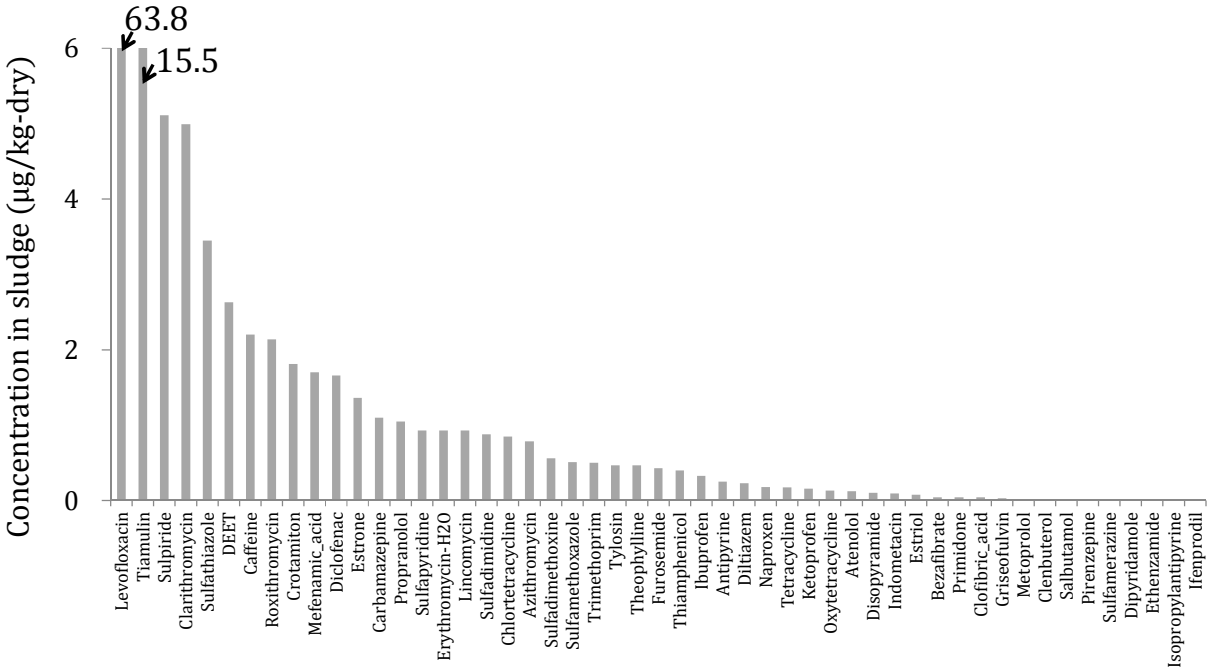

Figure 4.5 Detected concentrations of PPCPs and estrogens remaining in sludge

As there were no facilities recycling sludge in our study area, efflux into environment does not matter. However, there is a possibility that PPCPs or estrogens remaining in sludge may flow out into environment due to its recycling. Thus, for the basin environment with sludge recycling facilities, we should consider the possibility of their efflux into environment.

4.3.3 Mass balance

To determine percentage PPCPs and estrogens removal during wastewater treatment and to investigate their fate in STPs, target compounds in influent, effluent and dewater sludge were calculated and Equations 1 and 2 were used.

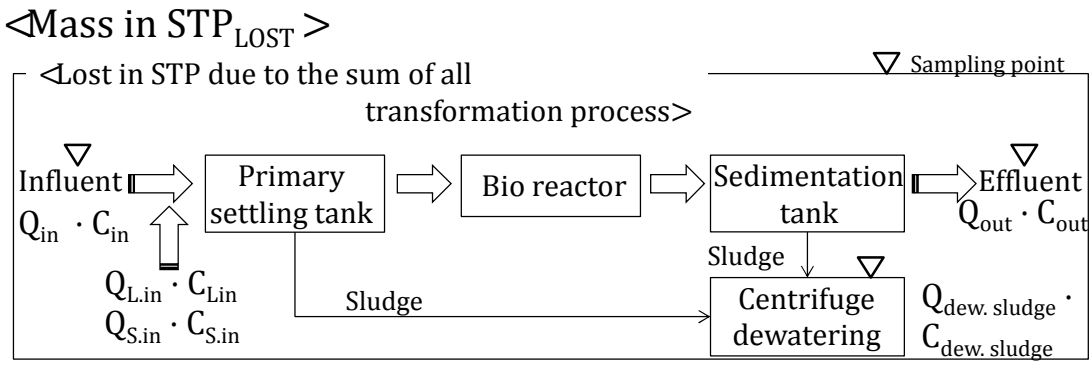

Figure 4.6 Sampling point of mass balance

Figure 4.6 shows the spots used for mass balance. Mass in effluent shows PPCPs and estrogens remaining in effluent, while mass in sludge indicates the result of samples collected from centrifuge dewatering. STP_{Lost} indicates PPCPs and estrogens removed at the entire process of wastewater treatment ranging from influent to effluent. Ratios of effluent, sludge and STP_{Lost} in STP-F by target compounds were shown in Figure 4.7. The amount of target compounds in the influent can be set at 100 percentages. Because these target compounds are partially degraded during wastewater treatment, those quantities are expressed in STP_{Lost}. Therefore the amount of target compounds remaining in the sludge, effluent,and must become 100 % STP_{Lost}.

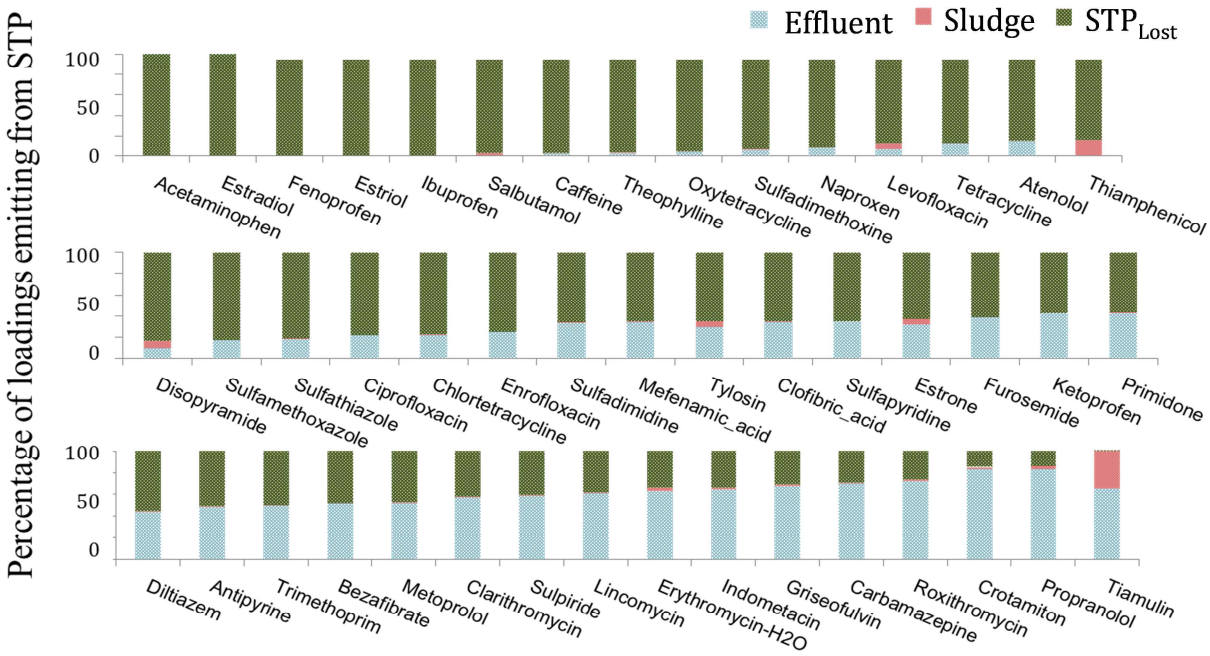

Figure 4.7 Mass balance of compounds in STP-F
(Influent is assumed 100%)

Research on PPCPs and estrogens remaining in effluent is increasing but research on the residual PPCPs and estrogens in sludge is not enough. Compounds such as disopyramide, estrone, levofloxacin, thiamphenicol and tylosin are adsorbed on sludge. Chlortetracycline, levofloxacin, sulfadimethoxine and thiamphenicol mainly used for VPs were adsorbed to sludge (Chlortetracycline 0.99 %, levofloxacin 6.21 %, sulfadimethoxine 0.70 %, thiamphenicol 15.38 %). Levofloxacin and thiamphenicol with high ratios in remaining by being adsorbed to sludge are higher than other compounds in likelihood to be discharged to environment. Livestock wastewater treated at STP-F is around 300 m^3/day, but for the whole area of Korea, it is around 4800 m^3/day (2012). Amounts of VPs remaining on sludge must be very high so it takes care to reuse the sludge. In reality, sludge at STPs is being used diversely in Korea. Though the sludge at STP-F is mostly incinerated, there are an increasing number of cases of reusing sludge in the world (Boxall A. B. A. et al., 2004; Sarmah A. K. et al., 2006; Kemper N. 2008).

4.3.4 Management of VPs

Figure 4.8 shows VPs sorted from livestock wastewater, PPCPs used by both humans and animals, concentrations of estrogens and removal efficiency at STP-F.

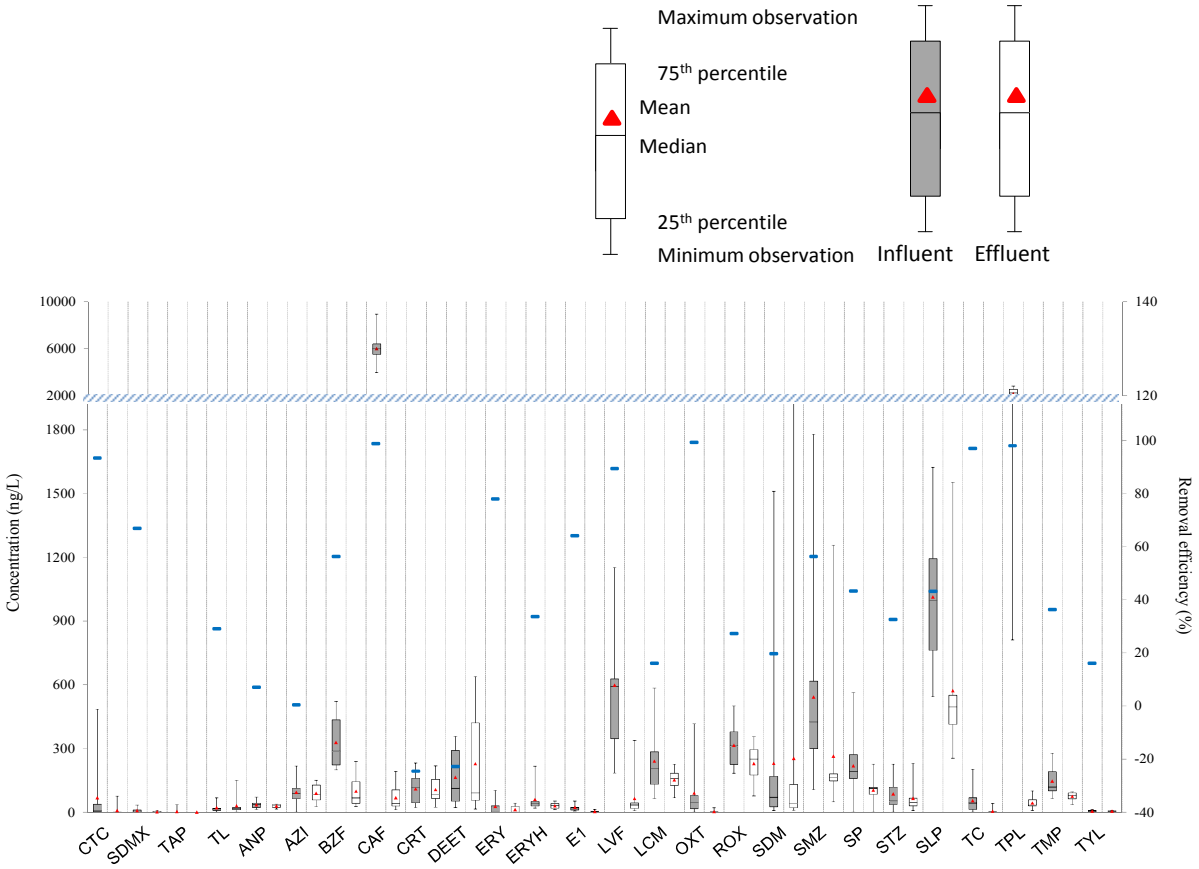

Figure 4.8 Concentration of VPs, pharmaceuticals (humans and animals) and estrogens and removal efficiency in STP-F

Chlortetracycline and sulfadimethoxine as VPs showed a mean removal efficiency of 99.3 % and 66.9 % existing at low concentrations in effluent. Tiamulin showed a low removal efficiency of 29 % and thiamphenicol existed below the limits of detection at STP-F. Considering Chapter III, tiamulin as VPs can be more effectively treated in A2O and MLE processes than in B3 process of STP-F. Besides, as to sulfadimethoxine chemical treatment using ozone is more effective than chlorine disinfection, while chlortetracycline and tiamuline can be effectively treated using UV. Among pharmaceuticals used by both humans and animals, DEET, roxithromycin and sulpiride with high concentrations in effluent showed low removal efficiency at STP-F. As verified in Chapter III, DEET is a substance with low treatment efficiencies for all processes. For roxithromycin and sulpiride, however, we can increase removal efficiency by adding UV or ozone process.

4.4 Conclusions

The STP studied in this Chapter is a facility that primarily treats livestock wastewater in HBR-II and then treats it with B3 process with wastewater. So analysis was made on PPCPs and estrogens included in livestock wastewater, excretions and sludge as well as influent and effluent of the STP.

1) The VPs detected chiefly in the STP include tiamulin, chlortetracycline, sulfadimethoxine and thiamphenicol, while pharmaceuticals used by both animals and humans were found to be enrofloxacin, estrone, oxytetracycline, tylosin, sulfadimidine.

2) There were 51 kinds of PPCPs contained in sludge, which included a large amount of VPs as well as levofloxacin, tiamulin and sulpiride. Above all, since sludge is reused diversely, PPCPs and estrogens contained in sludge can be leaked out to the environment and should be taken care of in their reuse. With no facilities to treat sludge in this study area, runoff of PPCPs and estrogens caused by sludge was not considered. If there are facilities to treat sludge near the river in another area, sludge should be considered in basin management without fail. Chlortetracycline, levofloxacin, sulfadimethoxine and thiamphenicol mainly used for VPs were adsorbed to sludge (Chlortetracycline 0.99 %, levofloxacin 6.21 %, sulfadimethoxine 0.70 %, thiamphenicol 15.38 %). Levofloxacin and thiamphenicol with high ratios in remaining by being adsorbed to sludge are higher than other compounds in likelihood to be discharged to environment.

3) Among VPs sorted from livestock wastewater, chlortetracycline and sulfadimethoxine showed a mean removal efficiency of 99.3 % and 66.9 % at STP-F, existing at low concentrations in effluent. Then, tiamulin showed a low removal efficiency of 29 % and thiamphenicol existed below the limits of detection at STP-F. Sulfadimethoxine and tiamulin with relatively low removal efficiency are considered to be VPs highly likely to flow out into the river.

4) In controlling VPs at Gyeongan River, care must be taken of sulfadimethoxine and tiamulin highly likely to be discharged. It was verified that chlortetracycline and tiamulin detected from the river are mostly introduced from the effluent of STP. That is, chlortetracycline and tiamulin require management using the model and are the substances considered to minimize contamination of the river by treating them effectively at STP.

Tiamulin as VPs can be more effectively treated in A2O and MLE processes than in B3 process of STP-F. Besides, as to sulfadimethoxine chemical treatment using ozone is more effective than chlorine disinfection, while chlortetracycline and tiamuline can be effectively treated using UV (Chapter III). Among PPCPs used by both animals and humans, for roxithromycin and sulpiride with a high concentration in effluent, we can increase removal efficiency with UV and ozone process (Chapter III). However, DEET, a substance with low removal efficiency, showed low removal efficiency at all STPs in the study area. As mentioned in Chapter III, however, using ozone or UV in the process of disinfection can also be a good way for effective management of PPCPs and estrogens.

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CHAPTER V

SEASONAL VARIATION AND CONCENTRATION OF PHARMACEUTICAL AND PERSONAL CARE PRODUCTS, ESTROGENS DETECTED IN THE GYEONGAN RIVER

5.1 Introduction

Various reports have been published on Pharmaceutical and personal care products (PPCPs) and estrogens in the last a few decades. PPCPs are important substances that are essential for treatment of disease as well as for improvement of health. Recently, the active ingredients in PPCPs and estrogens have increasingly been detected in a wide variety of environmental matrices. (Heberer., 2002; Smital et al., 2004; Kim et al., 2009; Li and Randak, 2009;). In Korea, Post-consumer Waste Medication collection and disposal project' began in earnest in 2010 (Park J. I. 2010). Potential pathways of PPCPs and estrogens into the environment include: discharge from factories, effluent from sewage treatment plants (STPs), direct inflow from aquatic fish farms and treatment of agricultural land with manure (Boxall et al., 2002; Halling-Sørensen et al., 2002). Among these routes, STP effluents are one of the most noteworthy sources of human PPCPs contamination in the environment (Clara et al., 2005). In addition, since the first concerns regarding potential adverse effects of PPCPs in municipal wastewater were expressed (Stumm-Zollinger and Fair, 1965), some of PPCPs have been linked to ecological impacts at trace concentrations (Daughton and Ternes, 1999). Besides, human and ecosystem health concerns derive from the fact that some PPCPs are known to cause cancer, mutations, and impede the reproduction and hormone function of living organisms (Liu et al., 2005; Han et al., 2006; Zhou et al., 2007; Selene et al., 2012).

Korea is a rapidly developed country and Seoul is the capital of the country. The Han River runs through the center of the Seoul Metropolitan Area. People in the area were where approximately 25 million people accounting or at 49 % of the Korean population (2013) live and use the river water as their drinking water source. The Han River is the confluence of the South Han River, the North Han River and the Gyeongan River. The flux from Gyeongan River contributes only 1.6 % of the Han Rriver's total flux, while it burdens a 16 % pollution load on the Han River.

The purpose of this chapter is to appreciate seasonal characteristics of water pollution and main substances with analysis on concentrations of PPCPs and estrogens inflowing to Gyeongan River. As mentioned in Chapter III and IV, PPCPs, VPs and estrogens influent to STP are treated in diverse processes, but some of them remain to be introduced in the river. Such PPCPs, VPs and estrogens continue to flow into the river. As PPCPs, VPs and estrogens move along the river, they earn additional inflow from other sources of pollution or reduce by diverse microorganisms, photolysis and adsorption. Gyeongan River is located in Gyeonggi-do, southeast of Seoul, Korea, and it flows into the Paldang Lake. This lake is an important drinking water source for populations

in the Seoul metropolitan area. So management of Gyeongan River is very important to minimize the contamination of Paldang Lake. Besides Gyeongan River locating around the metropolitan area continuously experiences land utilization changes and expects pollutants increase following development.

5.2 Materials and methods

5.2.1 Chemicals

This study analyses 61 PPCPs, three natural estrogens [estrone (E1), 17β-estradiol (E2), estriol (E3)] and one synthesis estrogen [17α-ethynylestradiol (EE2)] show in Table 3.1.

5.2.2 Sampling points

Gyeongan River is located in Gyeonggi province, southeast of Seoul, Korea, and it flows into the Han River. This River is an important drinking water source for populations in Seoul and metropolitan area. Gyeona River basin is covered by 60% forest, 16.7% by agricultural and 2.6% by livestock farms (KNSO. 2009). The River was selected because the river is an important source that involves STPs for treating livestock wastewater. Gyeongan River is 49.3 km in length and 639.1 km^2 in site area and about 48 tons of water supplies to Paldang Lake a day (Figure 5.1). The area adjacent to Gyeongan River has Gwangju and Yongin cities with about 280,000 in water system population. Population density of Gyeongan River is 2-fold compared to those of North Han River and South Han River and with constant increase of population, pollutants increase is expected. Sampling of PPCPs and estrogens was conducted a total of twelve times from August 2011 through January 2014.

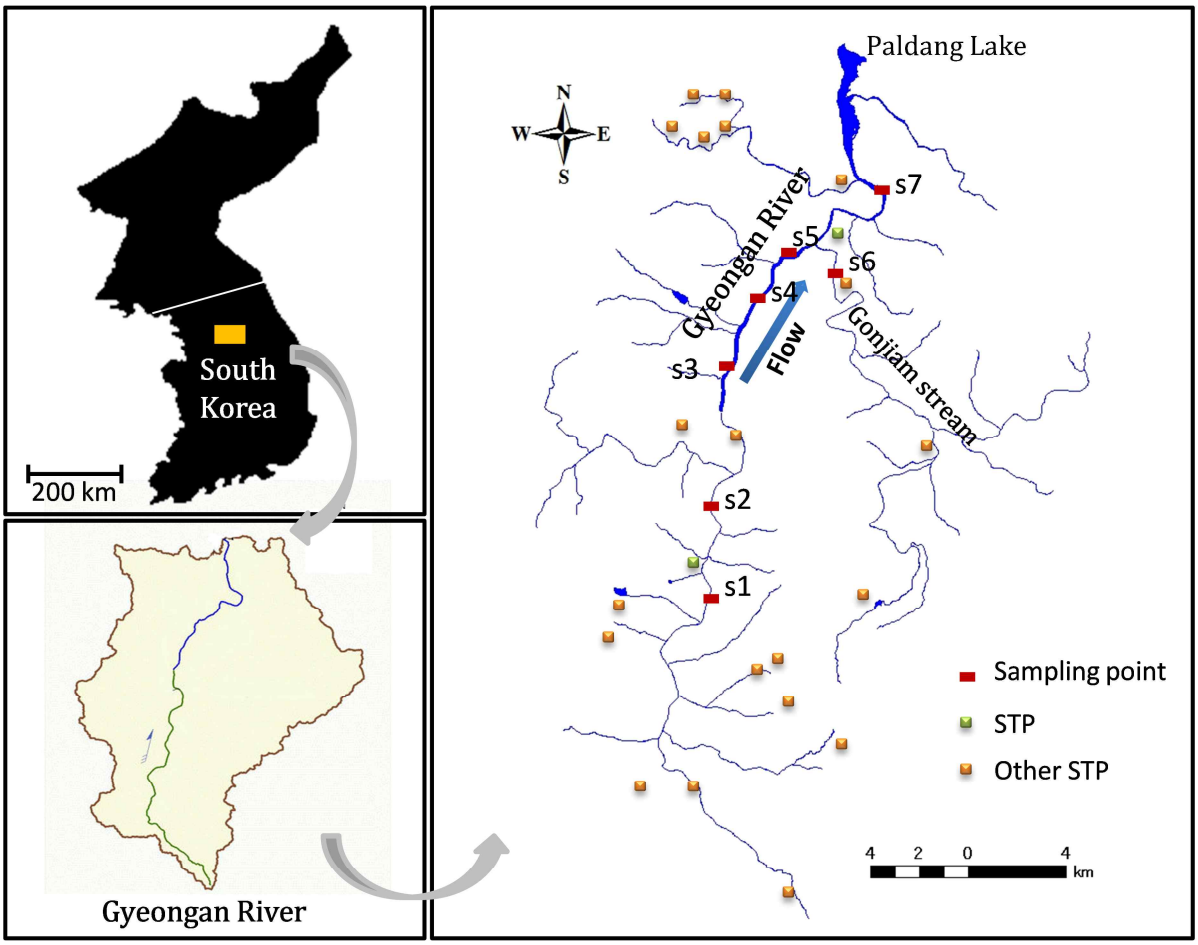


Figure 5.1 Location, STP and sampling points of Gyeongan River

5.2.3 Survey on the STPs and pollution source

Gyeongan River basin has dozens of large and small STPs and Figure 5.2 shows the treatment area as a representative plant.

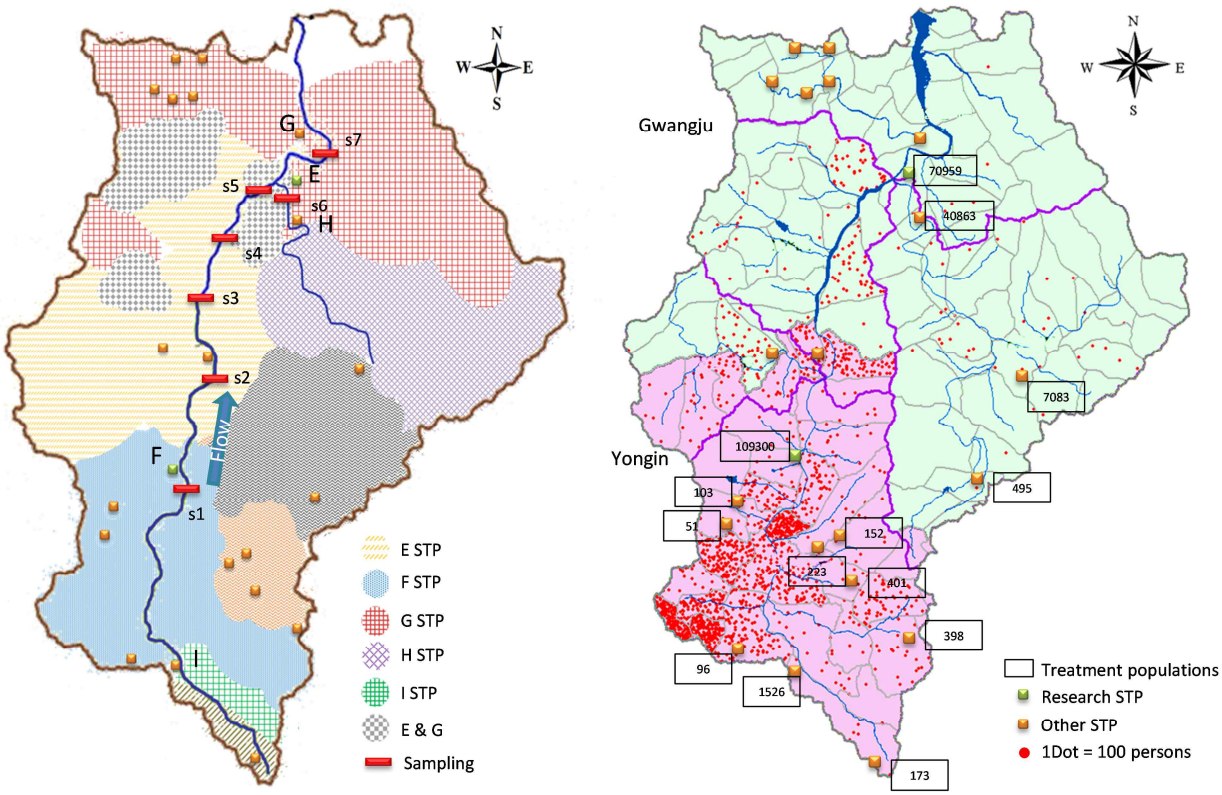


Figure 5.2 Treatment area of STPs located at Gyeongan River (left),
Treatment population of STPs describes the neighborhood of its location (right)

The STPs located along Gyeongan River covers residual area for Gwangju and Yongin cities, so we showed treatment population of each STP. Small STPs treat the wastewater occurring from less than 2,000 people. Effluents disposed of at such treatment plant are flowing in tributary or Gyeongan River directly. Accordingly, this study selected STPs expected to make the biggest influence on the PPCPs and estrogens contamination of Gyeongan River. Upstream of Gyeongan River live lots of small facilities and STP-F was selected for our subject of study because it has a large volume of treatment. Besides, there are three large-sized STPs in downstream areas of which STP-E was selected for our study with analysis of PPCPs and estrogens for a period of three years.

5.2.4 Reachability calculation

Reachability is the value that indicates the increase or decrease of chemicals when they are moving along a certain reach of a river. Reachability means the smaller a value, the bigger a reduction. Reachability of 100 % means there is no reduction in the section of river established.

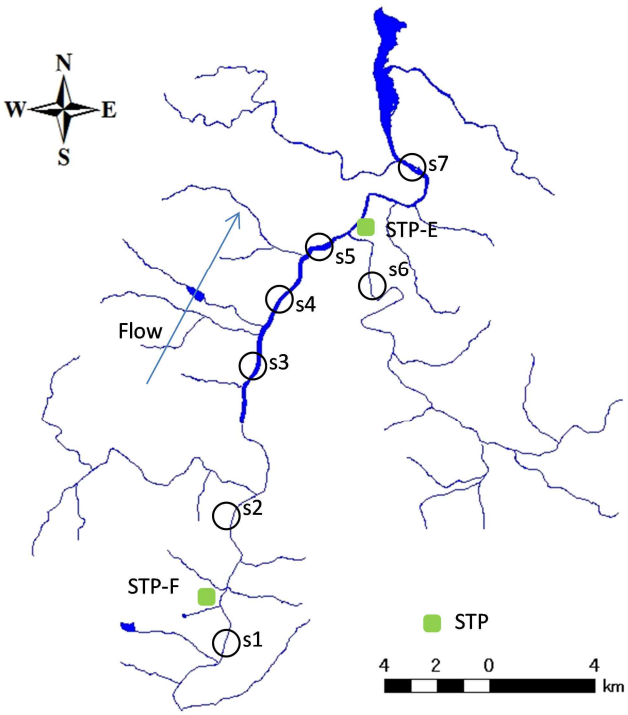


Figure 5.3 Locations of the STPs and sampling points on the Gyeongan River

By putting the section of Gyeongan River as shown in Figure 5.3, reachability and pollution load for each section of the river were estimated using equation 1 and 2.

$$r = \frac{C_d \times Q_d}{\sum(C_{sj} \times Q_{sj})} \times 100 \qquad eq\ 1$$

$$\text{Loading} = C \times Q \qquad eq\ 2$$

where r = reachability (%), C = concentration (ng L^{-1}), Q = Flow rate (m^3/s), d = Most downstream point in river, s = pollution load of river and j = pollution load ID.

s2 point is being the influx of effluent of STP-F, s7 points have been the influx of effluent of STP-E.

5.2.5 Assessment of hazard quotients

Figure 5.4 outlines the literature-based predicted no effect concentration (PNEC) values that were derived to assess the lethal toxicity of PPCPs and estrogens in aquatic organisms. These PNEC values were obtained from the NOEC (mg/L) and EC50 (mg/L) values of algae, bacteria, and daphnia. With the PPCPs and estrogen concentrations that were measured in the Gyeongan River (MEC) thus far, we calculated each hazard quotient (HQ) with equation 3.

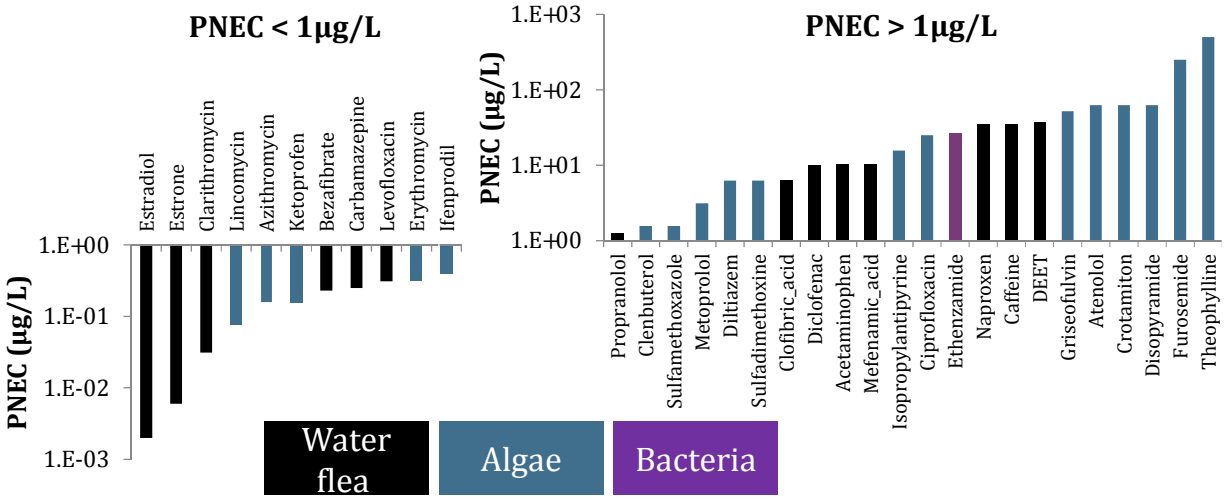


Figure 5.4 PNEC values of this research

$$HQ = MEC / PNEC \qquad eq\,3$$

HQ is defined by the US EPA as the ratio of the potential exposure to the substance and the level at which no adverse effects are expected (US EPA, 1997). If the HQ < 0.1, no adverse effect is expected. If 0.1 < HQ < 1, the hazard is low, but potential for adverse effects should be considered; and if 1.0 < HQ < 10, some adverse effect or moderate hazard is probable.

5.3 Results and discussion

5.3.1 Composition of PPCPs in Gyeongan River

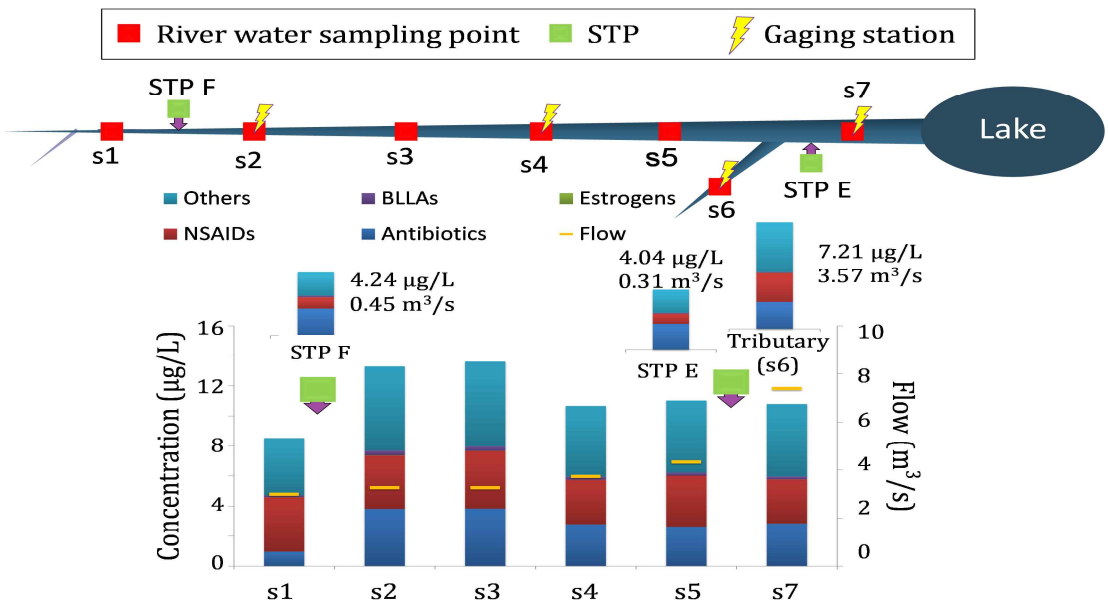


Figure 5.5 Composition of NSAIDs, antibiotics, estrogens and BLLAs of Gyeongan River

Similar to the research reports so far, Korean rivers also showed a high makeup of antibiotics and NSAIDs (MEK 2008). Among the detected antibiotics, clarithromycin, lincomycin, erythromycin, levofloxacin, roxithromycin, trimethoprim is a bacteriostatic antibiotic used mainly in the prophylaxis and treatment of urinary tract infections, and sulfamethoxazole is commonly used to treat urinary tract infections. Among the detected NSAIDs, acetaminophen, which is used as a fever reducer, ibuprofen and mefenamic acid, which are used as an anti-inflammatory PPCPs and a painkiller, and naproxen, which is antiphlogistics for arthritis, show high composition. Besides, BLLAs and estrogens, which showed a high composition in PPCPs and estrogens detected in many countries, showed a low composition in Korean rivers. However, accurate comparison was impossible because PPCPs and estrogens detected from reported papers and those in the present study are different in kind. PPCPs and estrogens detected in high concentration include carbamazepine (antiepileptic), caffeine (psycho-stimulant), atenolol, crotamiton, DEET, sulpiride and theophylline (beta-blocker).

5.3.2 Concentration of PPCPs and estrogens detected from river

From 2011 to 2014, a total of eleven-time sampling was made at Gyeongan River. For sampling, 6 points (s1-5 and s7) at Gyeongan River mainstream and 1 point (s6) at Gonjiam River, its biggest tributary, were surveyed. On the Table 5.1, for loadings of 61 PPCPs and 4 estrogens, a total of ten-time results were expressed in standard deviation, maximum and minimum except one sampling when there was a flood. As described previously, one of the objectives of this research was to apply the model in a manner that accounts for the inherent seasonal variability of Korean environments. Consequently, by sorting the flow rate of Gyeongan River for 2013 & 2014 by season, we put average flow value in Figure 5.6.

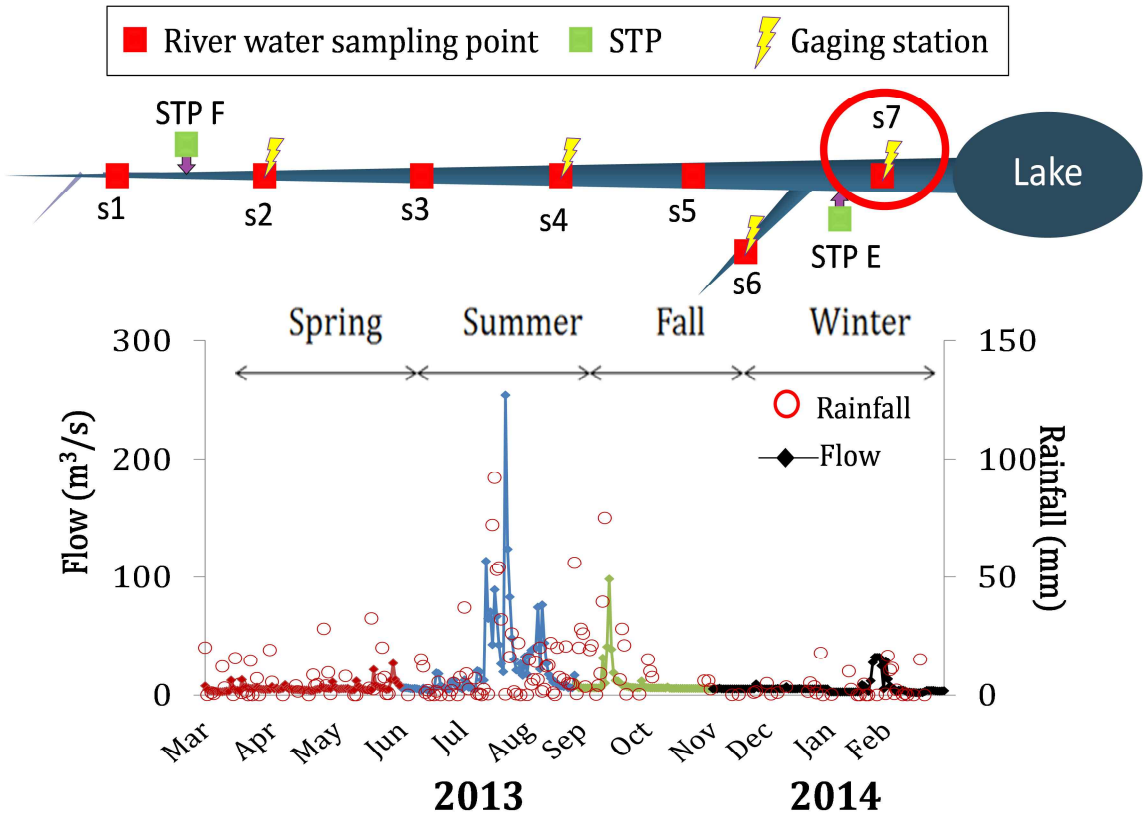


Figure 5.6 Flow rate of Gyeongan River (2013, 2014)

In Korea, there is much rain in the summer by seasonal characteristics, and Gyeongan River too showed a high flow rate in the summer with a mean flow rate of 11.15m^3/s. In 2013, the Figure 5.7 showed the concentrations of PPCPs and estrogens detected in s7 point of Gyeongan River showed 52 substances except for the LOD and LOQ.

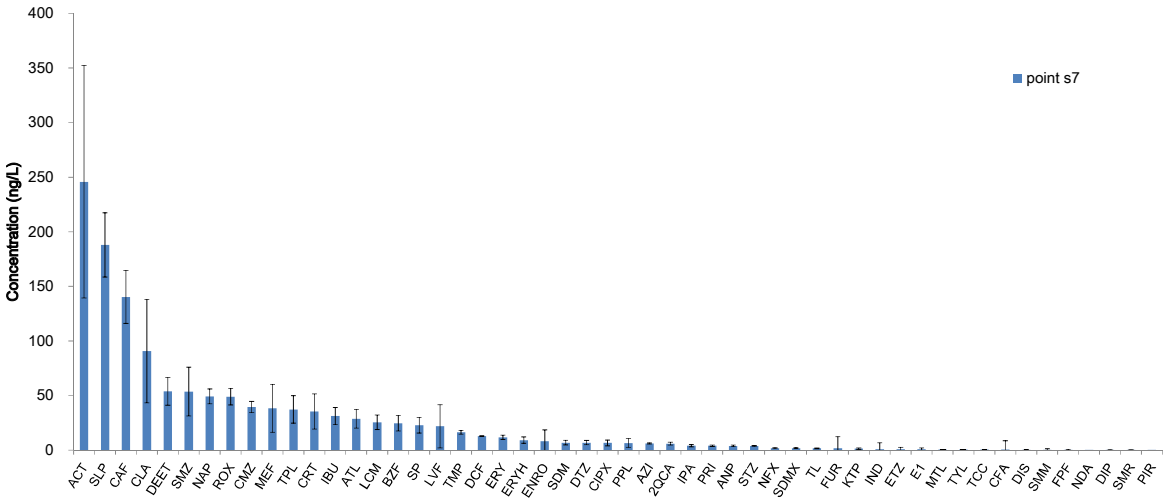


Figure 5.7 Concentration of PPCPs and estrogens in point s7 of Gyeongan River (2013)

Compounds detected in high concentration from point s7 of Gyeongan River include acetaminophen, sulpiride, caffeine, clarithromycin, DEET and sulfamethxazole etc. Besides, we looked into change in the river with effluents of two STPs located at Gyeongan River and PPCPs and estrogens introduced from tributary. Then, with regard to the seasonal flow rate in Figure 5.5 and substances detected with a high concentration at s7 point shown in Figure 5.6, we put the correlation in Figure 5.8.

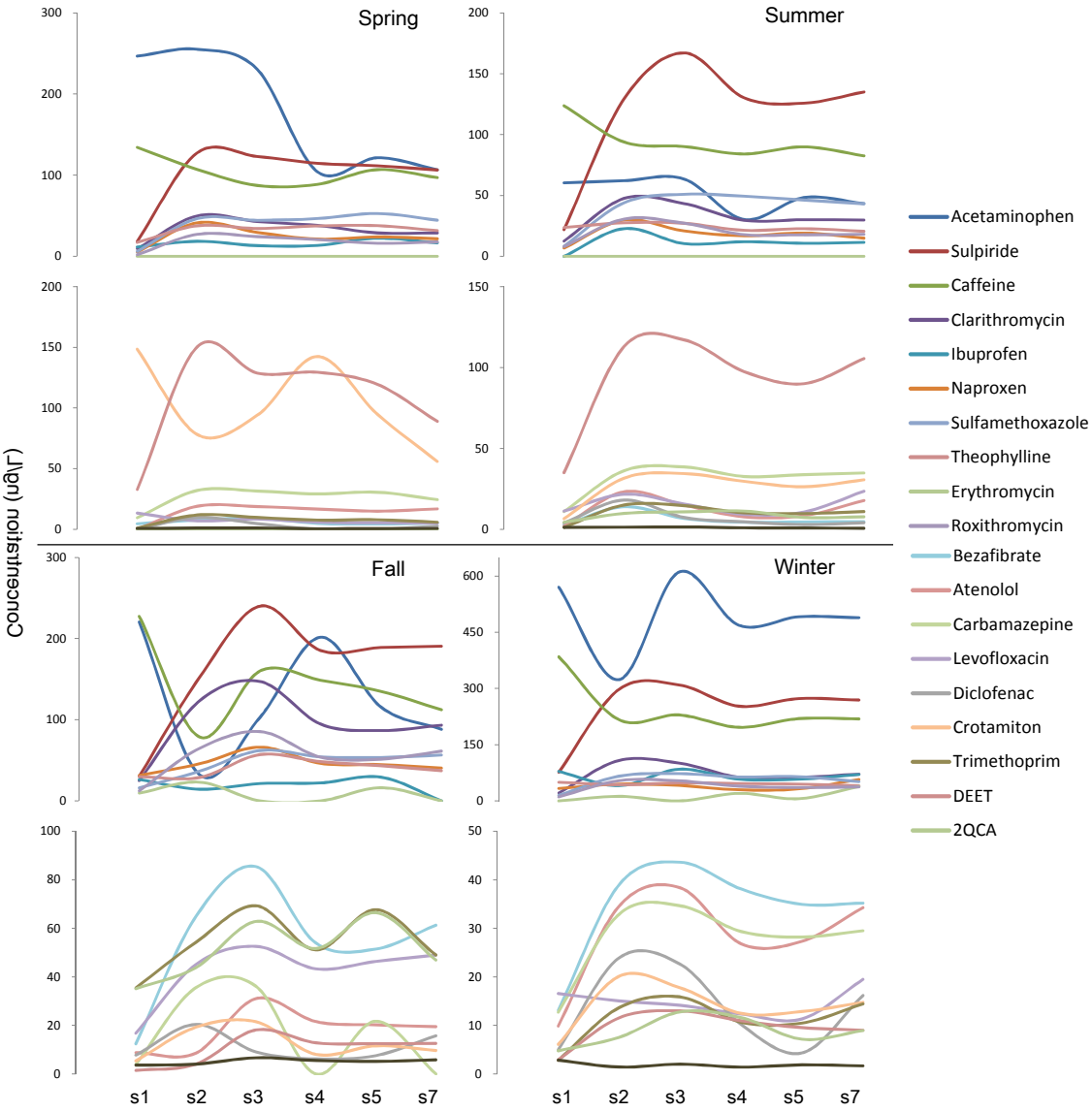


Figure 5.8 Seasonal change in the concentration of PPCPs and estrogens
(At s2 point effluent of STP-E and at s7 point, effluent of STP-E and tributary are flowing in.)

With verification of the change in concentration at s2 and s7 points, Figure 5.9 shows the concentrations of PPCPs and estrogens remaining in the effluent of STP-E and F and tributary (s6).

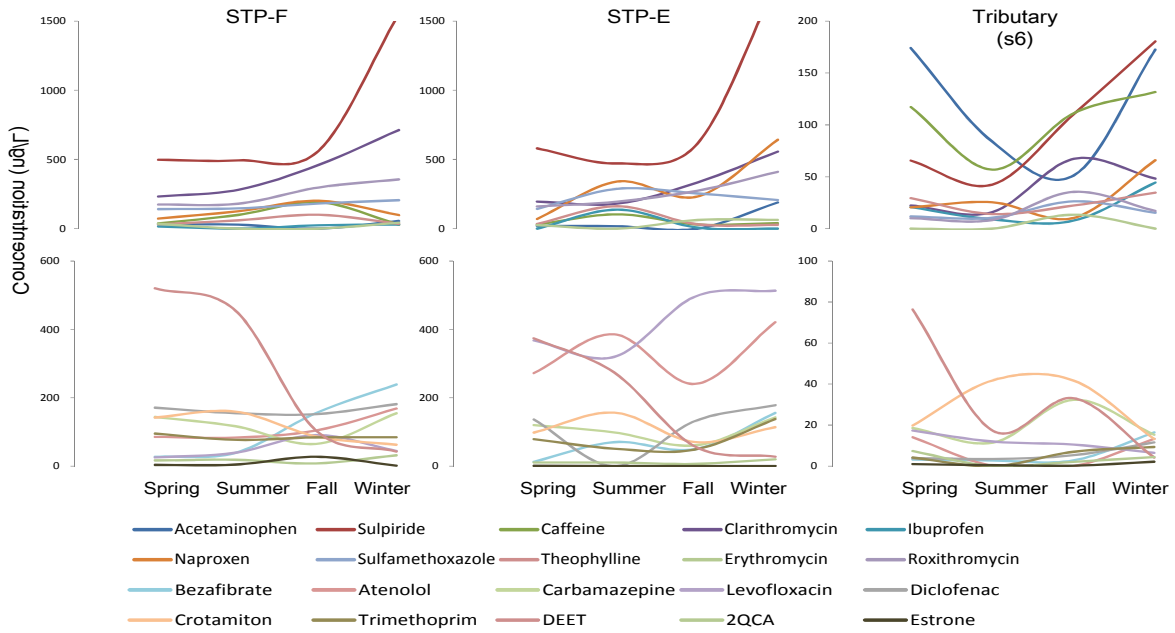


Figure 5.9 Seasonal concentrations of PPCPs and estrogens remaining in STP-E and F and tributary (s6)

For Gyeongan River, PPCPs and estrogens are being flowed in from point s1 and point s6, its tributary, in high concentration. In the upstream of point s1 are 9 large and small STPs where untreated PPCPs and estrogens seem to be coming in. In the upstream of point s6 located 2 large-sized STPs and 1 small-sized, where PPCPs and estrogens are being detected in high concentration. Between point s1 and s7 are the four STPs, of which two large-sized ones are included in the scope of the present study. At Point s2, where effluent of STP-F flows in, sulpiride, caffeine, atenolol and crotamiton etc. were detected. The s7, a point where effluent at s5, tributary (s6) and STP-E mix to flow, shows the highest mean concentrations of PPCPs and estrogens of all points. Besides, of VPs investigated in Chapter IV, tiamulin, chlortetracycline and sulfadimethoxine showed rapid increase at the point of introducing effluent from STP-F, while thiamphenicol was not detected from all points of the river. This study verified the change in the river by the influent of acetaminophen, sulpiride and caffeine etc. remaining in the effluent of STP and tributary (s6). Acetaminophen is the matter with high removal efficiency at STP and also reported to have been often detected at Gyeongan River as nonpoint source of pollution (Carlsson, C. et al., 2006). Besides, carbamazephine and crotamiton are the substance influent to river with a low removal at STP, by which we can verify the influent of sewage (Guang-Guo Ying. et al., 2009). Acetaminophen already existed at s1 in the river with a high concentration, with no change caused by the effluent from STP E and F found. It is also found that acetaminophen flowed into s6, a big tributary influent to Gyeongan River, contaminating the river. Carbamazephine and crotamiton increased in the concentration detected from the river at s2 and s7 by the inflow of effluent from STP, whereas there was no big change in concentration found for s2 to s5. To sum up, chief pollution sources of Gyeongan River are turned out to be the upstream of s1, upstream of s6 at its tributary, and STP E and F.

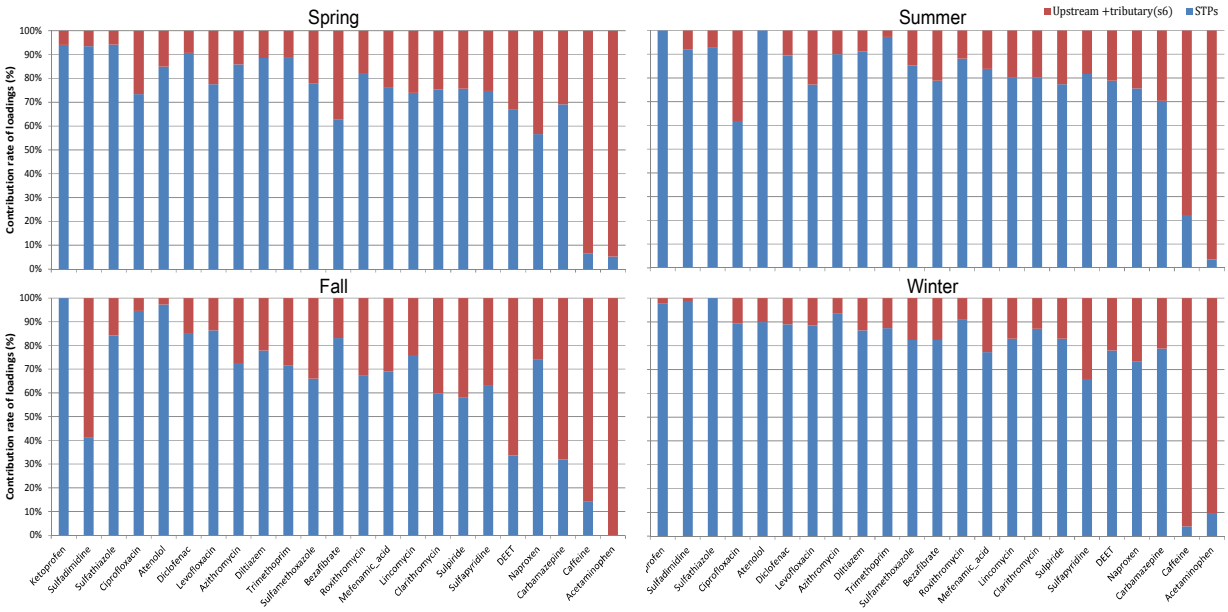
Table 5.1 Loading average (μg/s) and S.D. (standard deviation) of PPCPs and estrogens detected from each points of Gyeongan River

Loading ug/s

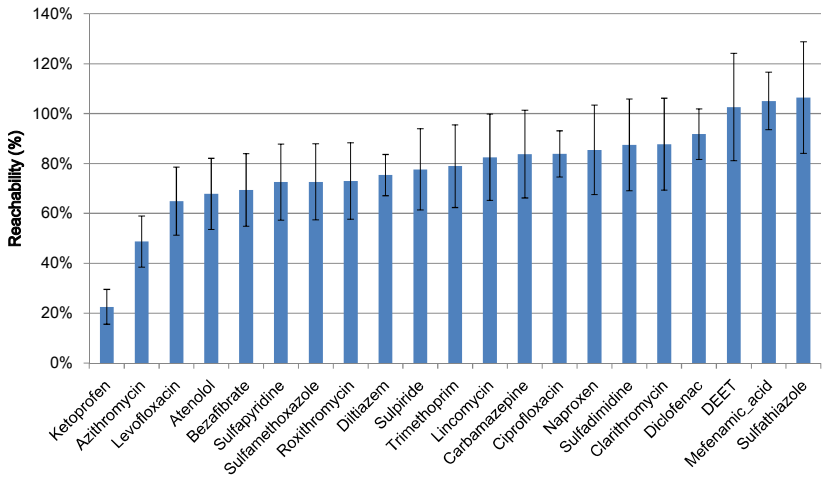
	s1				s2				s3				s4				s5				s6				s7			
	Average	SD	Max	Min	Average	SD	Max	Min	Average	SD	Max	Min	Average	SD	Max	Min	Average	SD	Max	Min	Average	SD	Max	Min	Average	SD	Max	Min
Acetaminophen	679.98	580.55	1957.86	68.53	466.13	369.38	1249.94	95.77	633.58	673.05	2357.79	53.09	497.78	415.92	1053.24	18.62	571.59	412.76	1436.85	73.05	405.76	458.28	1558.07	6.90	982.86	909.18	2796.42	208.34
Antipyrine	0.28	0.90	2.84	0.00	15.92	12.33	33.63	0.00	20.46	10.67	36.70	0.00	27.01	23.04	70.85	0.00	19.70	15.29	48.79	0.00	6.97	10.05	26.18	0.00	31.72	27.91	76.43	0.00
Atenolol	11.78	14.11	38.51	0.00	87.52	49.28	172.48	0.00	74.54	43.55	148.17	0.00	46.94	38.82	111.48	0.00	57.27	36.66	112.70	0.00	39.56	70.40	232.02	0.00	142.75	127.70	412.93	0.00
Azithromycin	5.32	2.96	11.66	0.00	26.99	18.12	72.51	10.89	15.83	9.09	34.26	4.62	12.77	8.76	32.65	2.10	10.92	8.72	32.43	0.00	23.73	34.95	113.85	0.00	31.37	30.03	103.88	0.00
Bezafibrate	26.73	14.80	49.12	1.80	80.32	55.09	197.08	25.48	83.33	59.98	201.58	23.96	60.65	44.60	153.01	11.93	56.51	43.02	147.54	6.12	20.43	27.40	91.74	0.18	110.86	102.21	324.37	10.93
Caffeine	672.42	360.32	1321.37	301.86	398.88	171.74	838.30	233.84	430.49	193.71	887.14	214.55	413.79	184.28	771.68	120.67	468.75	174.79	700.23	114.63	304.89	264.98	779.07	28.32	787.84	380.90	1405.60	183.88
Carbamazepine	40.06	14.38	68.67	16.60	141.50	42.92	211.67	75.63	146.32	45.95	231.73	68.73	139.07	62.87	228.60	48.90	141.61	66.36	240.61	49.68	105.71	100.86	332.78	11.93	295.34	154.50	613.06	113.82
Ceftiofur	0.13	0.40	1.25	0.00	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Chlortetracycline	N.D.	N.D.	N.D.	N.D.	11.56	32.31	103.04	0.00	5.31	16.80	53.14	0.00	1.58	4.99	15.78	0.00	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Ciprofloxacin	11.60	7.19	21.93	0.00	19.97	13.90	46.50	2.27	25.27	25.48	92.78	0.34	15.26	11.65	32.08	0.00	19.47	21.45	70.35	2.27	15.86	15.45	43.47	0.00	42.14	22.31	86.04	9.43
Clarithromycin	47.86	22.67	81.61	8.69	292.78	158.55	659.32	83.19	275.10	143.69	529.55	51.65	218.17	141.77	491.29	24.56	197.80	140.14	449.95	0.00	234.09	315.82	1060.81	0.00	492.15	405.21	1279.35	45.77
Clenbuterol	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.07	0.21	0.65	0.00	0.16	0.50	1.58	0.00	0.20	0.65	2.05	0.00	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Clofibric_acid	1.45	3.58	11.53	0.00	2.86	3.66	12.49	0.00	1.62	1.74	4.55	0.00	1.49	2.13	5.99	0.00	2.74	4.13	12.86	0.00	0.68	1.15	3.06	0.00	4.91	7.73	20.88	0.00
Crotamiton	78.01	141.50	476.02	8.89	117.00	76.21	283.44	23.59	126.59	93.16	340.86	24.88	171.88	252.14	858.61	17.07	149.85	176.68	572.04	17.65	107.24	90.84	291.94	25.18	250.57	210.43	649.64	69.42
DEET	56.87	48.87	145.16	5.32	214.36	242.40	615.73	29.10	198.95	200.45	544.26	17.56	220.19	256.03	780.61	10.15	214.58	242.72	720.55	10.22	89.38	98.41	297.88	5.81	360.86	383.19	1033.49	31.20
Diclofenac	8.38	8.33	20.42	0.00	51.88	28.40	92.37	7.77	37.85	27.00	87.39	2.72	22.75	19.89	61.08	0.00	26.98	34.65	110.96	0.00	33.61	41.22	140.34	0.00	66.03	56.55	176.51	0.00
Diltiazem	5.01	5.42	19.43	1.15	23.15	6.99	32.19	12.27	19.93	12.22	41.54	4.65	15.57	10.83	32.90	1.23	14.91	11.19	33.19	1.03	13.99	17.72	60.71	0.75	38.35	27.26	87.05	7.85
Dipyridamole	0.38	0.85	2.45	0.00	0.64	1.49	4.58	0.00	1.01	1.68	4.00	0.00	0.56	1.32	4.02	0.00	0.72	1.38	4.24	0.00	0.66	1.45	4.23	0.00	0.36	1.13	3.56	0.00
Disopyramide	1.70	3.96	12.65	0.00	0.37	0.80	2.51	0.00	0.38	0.79	2.48	0.00	1.58	3.61	11.51	0.00	1.72	3.64	11.67	0.00	1.77	3.17	8.35	0.00	1.20	2.52	7.24	0.00
Enrofloxacin	17.92	52.01	165.76	0.00	16.32	45.86	146.41	0.00	33.17	55.67	149.43	0.00	19.22	48.95	156.21	0.00	23.24	51.68	156.98	0.00	14.58	41.76	133.05	0.00	38.09	98.86	316.24	0.00
Erythromycin	17.62	30.81	97.78	0.00	38.26	35.29	94.89	0.00	50.91	150.17	477.88	0.00	37.91	58.11	182.79	0.00	33.34	43.06	124.78	0.00	28.34	36.56	93.91	0.00	54.36	62.69	181.85	0.00
Erythromycin-H2O	16.52	23.95	81.95	0.00	31.32	13.75	60.28	10.77	64.62	114.69	389.49	6.29	42.29	48.58	171.59	4.41	34.79	33.16	115.66	0.00	27.39	29.88	83.97	0.00	61.31	39.14	154.77	17.93
Estradiol	0.21	0.67	2.12	0.00	0.63	1.99	6.29	0.00	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.02	0.06	0.18	0.00	N.D.	N.D.	N.D.	N.D.
Estriol	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Estrone	3.13	3.14	9.75	0.00	3.27	2.18	6.33	0.00	3.29	2.59	7.79	0.00	2.79	1.90	6.34	0.00	2.47	1.57	4.33	0.00	2.30	1.77	5.14	0.00	4.83	3.45	9.17	0.00
Ethenzamide	1.04	1.84	5.97	0.00	3.19	3.23	9.56	0.00	3.32	3.23	10.16	0.00	2.99	3.03	7.65	0.00	3.04	3.59	10.59	0.00	2.59	3.99	12.70	0.00	6.26	6.66	19.09	0.00
Ethynylestradiol	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Fenoprofen	0.97	2.44	7.69	0.00	0.95	2.09	6.01	0.00	0.54	1.70	5.37	0.00	N.D.	N.D.	N.D.	N.D.	1.74	4.40	13.83	0.00	0.28	0.88	2.79	0.00	3.71	8.18	23.67	0.00
Furosemide	2.46	4.70	14.00	0.00	27.64	27.96	83.18	0.00	10.16	12.68	36.48	0.00	5.27	9.27	23.99	0.00	0.00	0.00	0.00	0.00	4.38	8.74	27.29	0.00	12.38	17.38	48.93	0.00
Griseofulvin	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.02	0.05	0.17	0.00	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Ibuprofen	98.49	78.30	269.95	0.00	101.15	51.06	177.01	38.65	106.74	84.89	326.97	47.72	79.67	40.75	154.23	20.92	99.23	51.59	151.83	0.00	57.49	50.78	162.17	0.00	145.17	111.94	331.47	0.00
Ifenprodil	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.00	0.00	0.00	0.00	0.44	1.39	4.39	0.00	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Indometacin	1.30	1.70	3.96	0.00	5.90	7.12	24.18	0.00	4.21	8.43	27.24	0.00	1.33	2.48	6.49	0.00	3.83	9.60	30.88	0.00	2.51	3.99	10.84	0.00	5.87	8.81	27.54	0.00
Isopropylantipyrine	2.25	2.06	5.24	0.00	15.79	19.39	69.93	4.44	14.57	4.96	21.23	4.85	16.90	10.58	41.79	5.06	15.31	10.49	38.89	3.09	5.35	7.22	23.28	0.20	25.84	21.22	67.90	5.14
Ketoprofen	0.89	1.50	4.60	0.00	2.11	3.50	9.51	0.00	1.31	2.84	8.96	0.00	0.13	0.40	1.27	0.00	0.55	1.39	4.37	0.00	0.80	2.04	6.43	0.00	5.97	16.00	51.22	0.00
Levofloxacin	24.07	19.06	56.87	0.00	48.35	27.67	100.83	13.90	32.21	21.48	72.70	9.29	24.43	13.59	45.17	2.99	27.66	13.28	52.23	7.72	38.01	41.62	123.99	0.00	101.14	86.41	253.13	26.32
Lincomycin	7.57	6.53	17.40	0.00	95.86	66.46	266.44	33.48	92.36	41.37	161.39	31.65	83.46	58.34	187.20	11.41	73.38	56.88	178.20	3.40	63.80	82.77	284.71	1.92	166.34	116.23	357.85	23.49
Mefenamic_acid	28.51	12.92	47.54	11.13	151.31	65.79	266.93	79.16	143.28	62.47	237.29	40.73	118.00	98.64	316.90	0.00	122.82	81.40	254.18	0.00	84.97	83.95	227.96	0.00	197.80	152.08	481.51	0.00
Metoprolol	1.11	2.30	7.33	0.00	2.70	3.29	10.52	0.00	2.93	3.41	8.71	0.00	2.74	3.58	11.13	0.00	2.42	3.41	8.38	0.00	2.54	3.55	8.79	0.00	4.59	6.03	17.96	0.00
Nalidixic_acid	1.27	2.76	8.77	0.00	1.12	1.90	5.17	0.00	2.28	6.42	20.43	0.00	3.60	6.46	19.59	0.00	2.53	7.30	23.23	0.00	0.23	0.74	2.33	0.00	0.91	1.91	4.65	0.00
Naproxen	66.30	40.26	140.65	16.84	166.48	81.16	347.52	78.21	139.82	78.45	314.81	67.04	114.67	78.96	240.22	34.99	119.12	73.52	240.87	36.42	88.04	73.69	250.90	11.64	242.48	187.41	625.01	66.57
Norfloxacin	3.12	8.02	25.70	0.00	3.44	6.04	16.59	0.00	7.54	17.86	54.98	0.00	3.71	6.93	19.49	0.00	8.39	19.72	60.46	0.00	3.20	8.89	28.29	0.00	9.72	16.73	42.68	0.00
Oxytetracycline	6.20	19.61	62.02	0.00	32.32	101.62	321.54	0.00	1.82	5.16	16.40	0.00	0.00	0.00	0.00	0.00	7.80	19.46	61.20	0.00	0.06	0.19	0.59	0.00	2.71	7.29	23.15	0.00
Pirenzepine	0.07	0.16	0.43	0.00	0.09	0.21	0.62	0.00	0.13	0.26	0.63	0.00	0.09	0.20	0.50	0.00	1.28	3.27	10.42	0.00	0.72	2.17	6.90	0.00	0.23	0.51	1.48	0.00
Primidone	1.44	3.08	8.21	0.00	6.70	8.62	22.30	0.00	8.26	11.13	28.18	0.00	8.91	11.77	27.92	0.00	9.03	12.71	31.45	0.00	2.25	5.82	18.66	0.00	21.95	24.31	69.78	0.00
Propranolol	2.36	2.67	8.56	0.00	21.50	10.20	36.34	7.62	18.02	10.62	30.41	3.31	12.54	9.73	29.69	0.20	10.92	10.06	31.61	0.02	15.52	20.77	67.15	0.00	33.34	30.93	98.44	2.55
2QCA	10.88	10.29	28.15	0.00	15.86	15.88	45.62	0.00	20.91	21.26	50.15	0.00	19.11	19.13	55.10	0.00	11.22	12.92	35.65	0.00	13.89	12.70	39.02	0.00	34.17	30.32	72.91	0.00
Roxithromycin	25.33	11.39	39.84	6.53	163.95	51.36	238.32	75.89	163.10	65.44	253.92	39.05	131.26	71.42	279.84	25.06	117.04	70.65	267.13	0.00	102.85	133.62	432.73	0.00	301.31	223.59	767.26	61.50
Salbutamol	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Sulfadimethoxine	0.25	0.40	0.97	0.00	2.55	2.95	7.40	0.00	4.70	5.50	15.42	0.00	6.56	9.92	25.48	0.00	6.52	9.77	27.79	0.00	0.38	0.62	1.45	0.00	9.07	15.14	47.81	0.00
Sulfadimidine	4.47	6.04	20.42	0.00	56.24	46.90	123.11	7.31	97.86	190.17	634.05	8.90	75.69	128.61	434.28	7.16	70.82	119.34	402.55	6.95	4.65	4.15	11.75	0.43	86.32	132.11	449.83	10.00
Sulfamerazine	0.32	1.01	3.20	0.00	0.16	0.51	1.60	0.00	0.19	0.41	1.11	0.00	N.D.	N.D.	N.D.	N.D.	0.01	0.03	0.10	0.00	0.14	0.43	1.37	0.00	0.76	2.09	6.63	0.00
Sulfamethoxazole	38.79	22.04	83.91	10.65	163.89	59.85	254.75	65.46	213.66	127.52	530.55	58.09	201.38	101.49	390.65	43.45	201.55	98.96	371.73	47.30	73.10	59.46	184.31	12.75	378.37	178.96	707.00	106.59
Sulfamonomethoxine	0.15	0.32	0.89	0.00	0.25	0.54	1.43	0.00	1.66	4.97	15.78	0.00	0.42	1.02	3.17	0.00	2.07	6.20	19.70	0.00	0.16	0.49	1.56	0.00	1.47	3.44	11.01	0.00
Sulfapyridine	45.91	55.28	182.40	0.00	89.09	60.81	171.16	0.00	78.74	57.88	153.91	0.00	74.76	61.10	171.71	0.00	71.32	49.76	148.02	0.00	44.73	45.33	151.41	0.00	159.95	137.76	456.73	0.00
Sulfathiazole	3.08	5.29	16.53	0.00	35.63	24.54	86.62	0.00	31.55	18.69	78.69	5.64	25.70	19.79	58.94	0.00	24.87	18.72	51.77	0.00	6.19	5.39	14.43	0.00	29.19	23.56	70.16	0.00
Sulpiride	76.50	70.58	262.82	0.00	548.76	243.96	1148.75	308.15	584.39	271.32	1196.49	294.40	505.13	221.73	961.78	231.26	487.58	251.01	980.73	76.77	387.75	289.81	930.47	20.20	1127.57	570.52	2385.46	239.44
Tetracycline	N.D.	N.D.	N.D.	N.D.	2.18	6.24	19.86	0.00	2.52	7.96	25.16	0.00	N.D.	N.D.	N.D.	N.D.	0.72	2.28	7.20	0.00	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Theophylline	85.69	46.87	171.22	21.49	112.44	33.82	166.22	51.16	119.28	41.60	186.00	44.49	123.50	68.79	250.60	28.03	128.24	62.08	227.60	27.40	82.45	64.56	214.22	12.46	219.35	126.85	466.18	52.83
Thiamphenicol	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.98	3.09	9.76	0.00	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Tiamulin	1.98	3.98	13.15	0.00	13.05	12.73	44.51	2.18	11.63	14.02	43.81	1.60	9.54	11.36	33.61	0.82	7.66	9.69	26.81	0.37	1.52	2.50	8.28	0.00	10.67	14.99	38.45	0.00
Triclocarban	21.97	16.91	54.55	0.00	18.88	22.31	60.83	0.00	31.06	32.68	94.40	0.00	15.91	18.53	62.23	0.00	12.55	15.97	49.14	0.00	14.85	18.14	56.73	0.00	24.70	33.65	101.26	0.00
Triclosan	5.07	16.04	50.72	0.00	9.53	20.87	59.62	0.00	11.62	16.72	39.60	0.00	10.83	22.66	69.65	0.00	0.94	2.97	9.38	0.00	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Trimethoprim	5.38	6.68	22.34	0.00	42.83	21.81	80.01	11.99	46.08	22.22	74.97	8.69	34.49	20.76	66.48	1.80	33.45	20.50	64.82	3.60	32.57	45.14	152.65	0.00	83.67	61.73	211.05	0.00
Tylosin	3.24	5.00	15.90	0.00	2.32	2.66	6.91	0.00	3.87	5.69	18.73	0.00	2.28	4.70	15.15	0.00	2.98	5.06	14.76	0.00	2.07	3.71	11.81	0.00	5.53	6.22	17.36	0.00

5.3.3 Reachability

The following shows the reachability of PPCPs in the section of river. However, reachability was calculated as shown in Figure 5.10(A) on the subject of 16 substances, excluding acetaminophen and caffeine with a high load at upstream and tributary as a major source of drawing off PPCPs on the river basin. We verified reachability of target compounds by season to compare (Figure 5.10(B)).



(A)



(B)

Figure 5.10 (A) Contribution rate of loadings (B) Reachability of PPCPs in Gyeongan river

With no distinct change in the difference of loadings by season (Fig 5.10 (A)) found, reachability was put using the mean value. Lincomycin, carbamazepine, ciprofloxacin, naproxen, sulfadimidine,

clarithromycin, diclofenac, DEET, mefenamic_acid and sulfathiazole showed the reachability of around 100% with little decrease found in Figure 5.10(B). However, substances such as ketoprofen, azithromycin, levofloxacin, atenolol and bezafibrate showed low measurement of reachabilities proving their decrease in the reaches of this section. This can suggest the result of the ketoprofen, azithromycin, levofloxacin, atenolol and bezafibrate being influenced by photolysis, biodegradation and/or adsorption by river sediments in the course of river flow. Using the reachability of PPCPs, we can identify the compounds coming from influent of STPs or pollution sources. In addition, from reduction of reachability it is known that PPCPs are reducing at a river because of photolysis, biodegradation, and adsorption. Accurate modeling requires an experiment on how much each of PPCPs is affected by photolysis, biodegradation and adsorption. Chapter VI sorted ketoprofen and levofloxacin into substances easily influenced by photolysis, while verifying that azithromycim and bezafibrate are under the influence of biodegradation.

5.3.4 Seasonal variation in river

PPCPs and estrogens detected from Gyeongan River were compared between the summer and winter to grasp their characteristics (Figure 5.11). Left vertical line represents the loading of PPCPs and estrogens in winter, and the horizontal line represents loading of PPCPs and estrogens in summer. Compounds detected in the summer in high concentration include antipyrine (painkiller), crotamiton (remedy for itch), DEET (insect repellent), ethenzamide (anti- inflammatory) and primidone (remedy for epilepsy). On the other hand, the compound detected in high concentration in the winter was found to be acetaminophen, bezafibrate, chlortetracycline, norfloxacin (urinary tract infections), sulpiride, tetracycline, thiamphenicol and tiamulin.

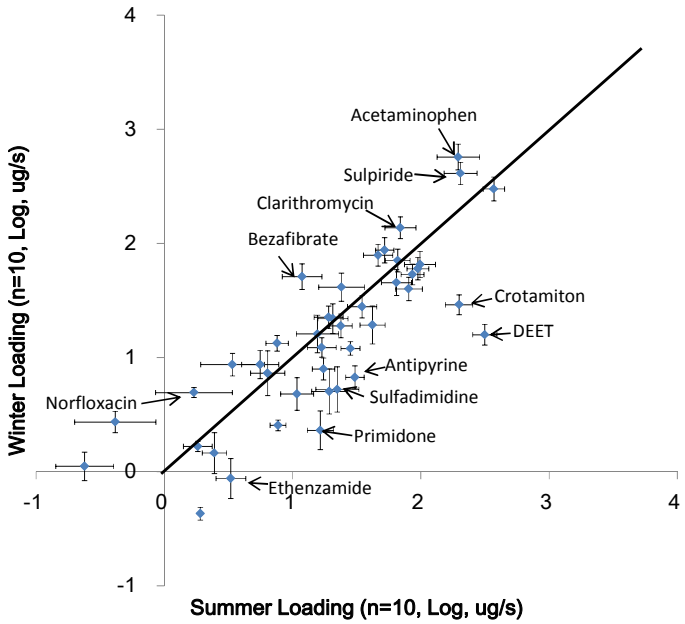


Figure 5.11 Comparison of PPCPs and estrogens detected in summer and winter from Gyeongan River

Correlation was verified between PPCPs and estrogens detected from the river and removal efficiency of the STPs. When comparing PPCPs remaining in the effluents of STP and the river between summer and winter, it showed a similar tendency. PPCPs detected in the summer from effluent were DEET, crotamiton, sulfadimidine and triclocarban, which are similar to the case of river. PPCPs detected in the winter from effluent were very similar to those chiefly detected from the river, too. Since PPCPs and estrogens introduced from STPs make a large influence on the river, increasing removal efficiency at STPs can reduce the river contamination.

5.3.5 PPCPs and estrogens flowed in the river from wastewater treatment facilities outside of the surveyed area

Although made on the subject of Gyeongan River, this study has failed to cover the upstream area of s1 and s6 (Figure 5.12). As the result of survey, however, many portions of pollution sources influent to Gyeongan River were flowing in from the excluded area. Figure 5.13 shows the average loads for each spot in an effort to verify how much PPCPs and estrogens are flowing in from others than this study area (s1, s6).

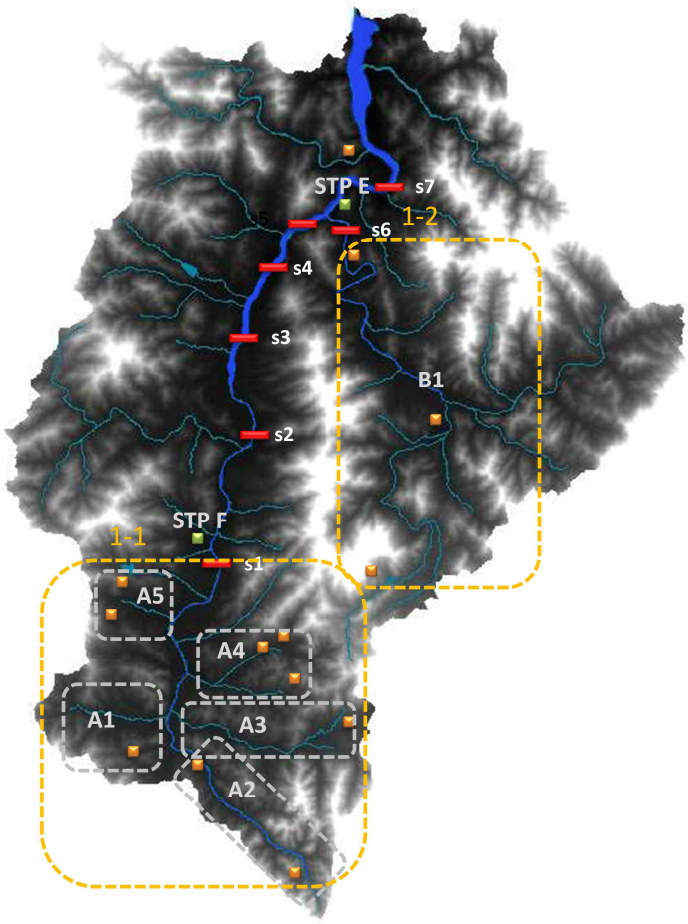


Figure 5.12 Wastewater treatment facilities outside of the surveyed area

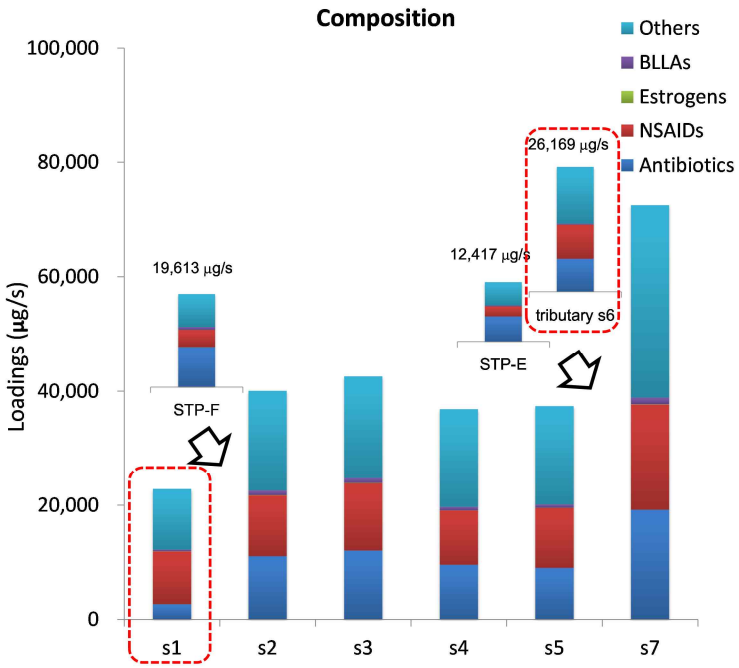


Figure 5.13 Loading of PPCPs and estrogens flowing in from s1 and s6

Though there are many small rivers at the study area, we left them out because only small amounts of flow rate are flowing in, except s6. In 1-1 area, there are nine small treatment plants as shown in Figure 5.13 and Table 5.2. Sampling was conducted from A5 of 1-1 area while Table 5.2 shows the number of STPs located at each point. Treatment plants located on 1-1 was chiefly dealing with the domestic sewage collecting septic tanks with vehicle and disposing mostly at STP-F (Figure 5.12). 1-1 area is mountainous and it is treating sewage with small treatment plants for area without a sewers system. There are 9 of such facilities and treated effluents are flowing in Gyeongan River. A1 area has one small treatment plant with a treatment capacity of 20 m^3/day, A2 area use treating sewage with MBR and SBR (sequencing batch reactor) processes, respectively. SBR are a special form of activated sludge treatment in which all of the treatment process takes place in the reactor tank and clarifiers are not required. A3 area has a treatment plant in new biosorption system (NBS) process, A4 two MBR and one NBS treatment plant, A5 treatment plants in SBR and MBR processes. NBS is a method of removing phosphorus and nitrogen in sewage using adsorption of organic matters from microbes and reaeration (Figure 5.14). Flow rate was measured with sampling at each influent point of effluent water from STPs, the result of which is shown in Figure 5.12.

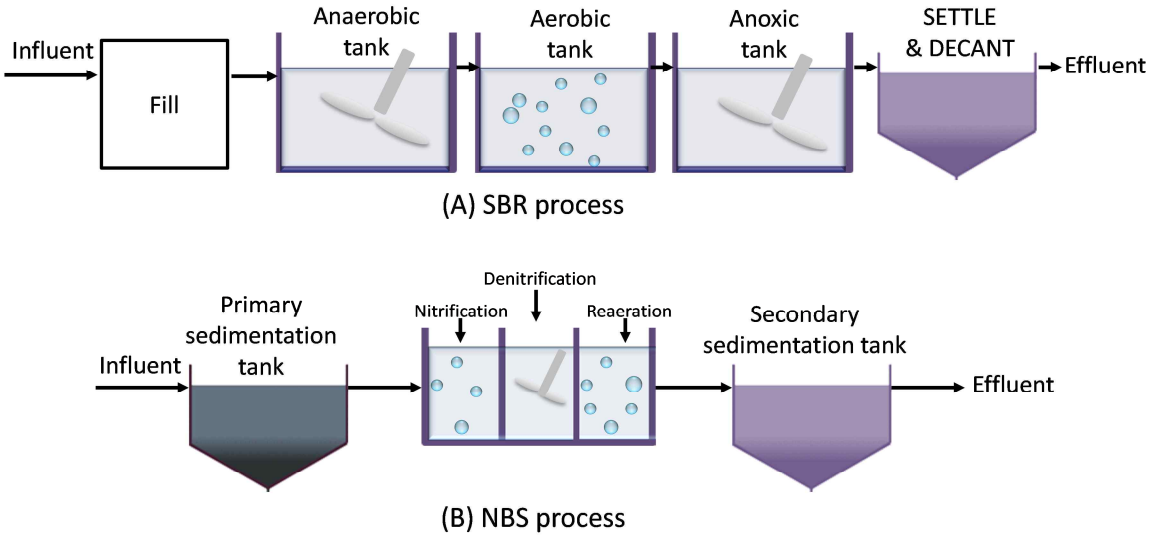


Figure 5.14 (A) Sequencing batch reactor (SBR) process (B) new biosorption system (NBS) process

Table 5.2 Characteristics of STP located at 1-1

Area	Number of STPs	Actual treatment capacity (m^3/day)	Biological treatment
A1	1	20	Advanced treatment
A2	2	454, 37	MBR, *SBR
A3	1	48	*NBS
A4	3	34, 84, 64	MBR, MBR, *NBS
A5	2	14, 21	*SBR, MBR

*New Biosorption System *Sequencing Batch Reactor

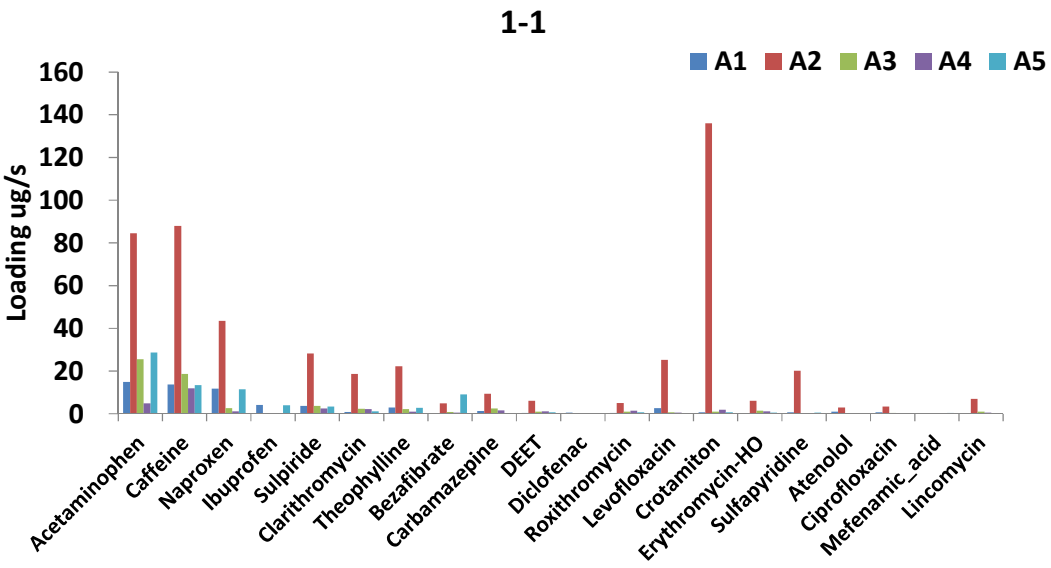


Figure 5.15 Comparison of loadings of PPCPs and estrogens from A1 to 5 on area 1-1

Out of 65 PPCPs and estrogens, 20 compounds detected with high concentration were chosen to be put onto the graph. Though acetaminophen and caffeine are the compounds with high removal efficiency at STPs, their discharge was observed from plants A2 to A5. The rest compounds were discharged to the river at plants in A2 to A5. Plants A2 to A5, which are treating wastewater with MBR and SBR method, respectively, are considered to have a problem in removing PPCPs. Though perfect accuracy required examination on the influent and effluent, this process was skipped in this study.

At 1-2 area are two STPs located with capacity of 4,000 m^3/day and 130 m^3/day. Sampling was conducted choosing the point in adequate mixture with effluents from both STPs.

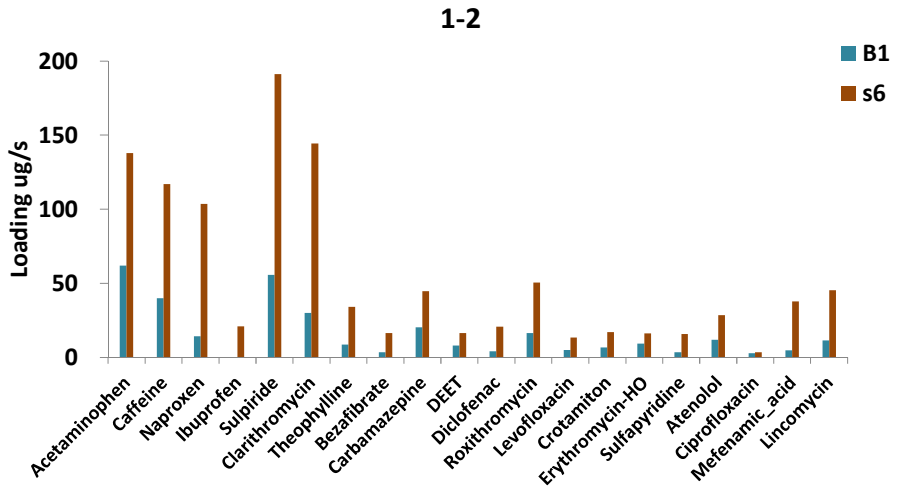


Figure 5.16 Loading of pollution sources of PPCPs and estrogens detected from the 1-2

Though the size of STPs on I-2 area is larger compared to those on 1-1 area, detected PPCPs were lower than 1-1 and diverse compounds were detected. It is considered because each STP uses different methods of treatment including chemical treatment.

5.3.6 Hazard quotients for PPCPs and estrogens in Gyeongan River

We calculated the HQs with the concentrations that were measured at each survey station in the Gyeongan River between 2011 and 2014. Figure 5.17 shows the HQs of the substances with HQs of 0.1 or higher in most survey stations, namely, carbamazepine, clarithromycin, erythromycin, estrone, and lincomycin. HQs were observed to increase at stations s2 and s7 that were exposed to the influents of sewage treatment plants (STPs). In addition, the HQs tended to increase in low-temperature seasons compared to high-temperature seasons.

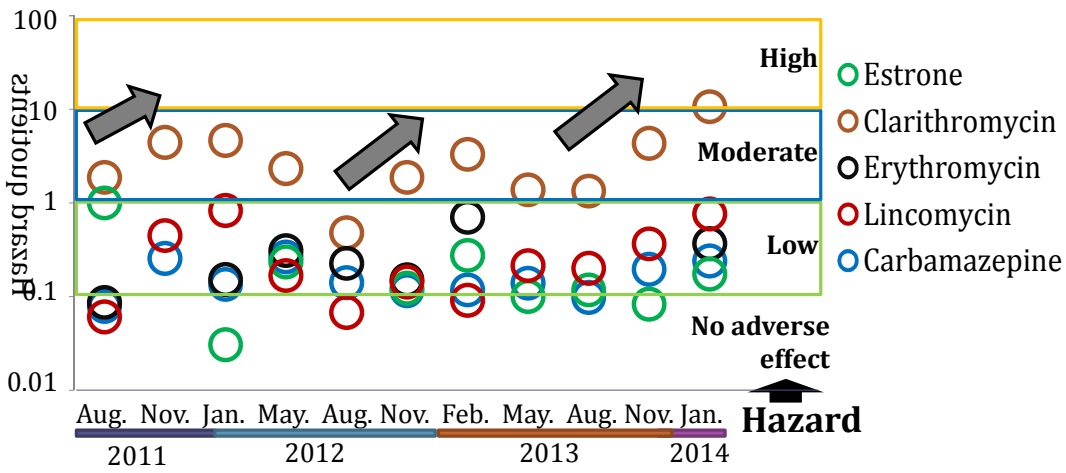


Figure 5.17 HQs for PPCPs and estrogens in Gyeongan River (s7 point)

Clarithromycin exhibited the highest HQ in the Gyeongan River. Clarithromycin is an antibiotic useful for the treatment of a number of bacterial infections. It is a macrolide antibiotic used particularly for respiratory infections, skin infections and Lyme disease. Its HQs were high in all of the survey stations of the Gyeongan River. These high HQs were attributable to its high concentrations in the effluents into the Gyeongan River, where were a result of the low removal rates in STPs. The second highest HQ was demonstrated by lincomycin. Lincomycin is a lincosamide antibiotic that comes from the actinomyces Streptomyces lincolnensis. Lincomycin, like carbamazepine, is also discharged into the Gyeongan River because it is untreated in the STPs.

The remaining three substances showed similar HQs. They were erythromycin, which is an antibiotic useful for the treatment of a number of bacterial infections; estrone, which is a type of estrogen; and, finally, carbamazepine. Carbamazepine is an anticonvulsant and mood-stabilizing drug used primarily in the treatment of epilepsy and bipolar disorder, as well as trigeminal neuralgia. It was identified to be a carcinogen in rat experiments, and toxicity experiments have shown that it is lethal to fish and daphnia at low concentrations.

5.4 Conclusions

At Gyeongan River, an important river influent to Paldang Lake, are located large and small STPs.

1) Acetaminophen is flowing in the river at s1 with high concentration while carbamazephine and crotamiton are flowing in due to the effluent of STP E and F. Among the detected antibiotics, clarithromycin, lincomycin, erythromycin, levofloxacin and roxithromycin. Trimethoprim is a bacteriostatic antibiotic used mainly in the prophylaxis and treatment of urinary tract infections, and sulfamethoxazole is commonly used to treat urinary tract infections. Among the detected NSAIDs, acetaminophen, which is used as a fever reducer, ibuprofen and mefenamic acid, which are used as an anti-inflammatory PPCPs and a painkiller, and naproxen, which are

antiphlogistics for arthritis, show high composition.

2) Besides, the compounds detected in high concentration from all points are acetaminophen, caffeine, DEET, sulfamethoxazole and sulpiride. For PPCPs and estrogens by season, antipyrine, crotamiton, DEET, ethenzamide, primidone and sulfadimidine were detected in the summer in high concentration while in the winter acetaminophen, bezafibrate, chlortetracycline, fenoprofen, norfloxacin, sulpiride, tetracycline, thiamphenicol and tiamulin were characteristically detected in high concentration.

3) Besides, of VPs investigated in Chapter IV, tiamulin, chlortetracycline and sulfadimethoxine showed rapid increase at the point of introducing effluent from STP-F, while thiamphenicol was not detected from all points of the river.

4) Risk evaluation results, concentrations and removal efficiencies of clarithromycin remaining in the effluent of STPs for the research period shows why hazard quotients (HQ) is high in fall and winter. Its HQs were high in all of the survey stations of the Gyeongan River. The second highest HQ was demonstrated by lincomycin. The remaining three substances showed similar HQs. They were erythromycin, which is an antibiotic useful for the treatment of a number of bacterial infections; estrone, which is a type of estrogen; and, finally, carbamazepine.

Results of comparing compounds detected from the effluents of STP and the river showed that untreated PPCPs and estrogens are polluting the river. Therefore, it requires the proper process at a STP to treat PPCPs and estrogens as well as constructing a model for management of river basin from PPCPs and estrogens.

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CHAPTER VI

MODEL CONSTRUCTION AND INSTALLATION OF FACTORS PREDICTION OF PPCPS AND ESTROGENS AT GYEONGAN RIVER

6.1 Introduction

Pharmaceuticals and personal care products (PPCPs) are chemicals used widely for daily treatment and prevention of many diseases (Metcalfe CD. et al., 2003; Carrara C. et al., 2008). The resulting presence of these substances in the aquatic environment can exert diverse negative effects on exposed organisms such as rotifera, shellfish, fish and batrachian (Picazo et al., 2010; Porter et al., 2011). Such PPCPs and estrogens are being flowed into the sewage treatment plants (STPs) for their process by various treatment processes but those untreated are introduced to a river (Bikram Subedi et al., 2014; Kolpin DW. et al., 2002; Lissemore L. et al., 2006; Miao XS. et al., 2002). And they have been identified as significant chemical pollutants in the river or stream. Previous researches of industrial nations have reported detectable amounts of PPCPs and estrogens in surface water, ground water and the water of STPs (Carrara C. et al., 2008; Godfrey E. et al., 2007). Generally, PPCPs and estrogens detected from the environment showed low concentrations similar to those of ng/L and μg/L detected from Korean rivers (Shishir Kumar Behera et al., 2011; Yeomin Yoon et al., 2010). However, at the low concentrations, the continual discharge of these chemicals in the environment may induce negative health effects on aquatic fauna and flora, such as feminization of various species (Dahms et al., 2011; Locatello et al., 2009; Porter et al., 2011; Zhenhua Yan et al., 2012). Therefore, the fate and transport of PPCPs and estrogens in varying environments has emerging as an important research (Barcelo D. et al., 2007). Identification and detection of PPCPs and estrogens in the aquatic environment requires highly sensitive instruments that consume considerable endeavor, time and money. Therefore, there has been an increasing interest in the development of models capable of reliably predicting the fate of PPCPs and estrogens. Typical models for predicting PPCPs concentrations include Pharmaceutical Assessment and. Transport Evaluation (PhATE) and Geography-referenced Regional Exposure Assessment Tool for European Rivers (GREAT-ER). PhATE much used in the US was developed by Pharmaceutical Research and Manufacturers of America (PRMA) as an instrument for evaluating the concentrations of active medical substances (Anderson et al., 2004; Feijtel T. et al., 1997). Similarly, GREAT-ER was developed as a means to predicting the concentration of chemicals in water and finding the distribution of concentration of such compounds at the surface water in Europe (Cunningham VL. et al., 2008; Robinson PF. et al., 2007; Schowanek and Webb, 2002). These models can be used to estimate the potential risk of chemicals in the aquatic environment (Hannah R. et al., 2009). However, Developed for the use in the US and UK, PhATE

and GREAT-ER have limitations in being applied to Korean rivers. Effective basin management requires understanding the inflow and movement of pollutants. It is the more important because Gyeongan River in Korea is important as the one flowing into sources. Therefore, prediction of accurate concentrations and effective management of PPCPs and estrogens require the review and revision of models. The final aim of this modeling was to predict the concentrations of frequently detected PPCPs and estrogens on the Gyeongan River basin using the model. Additional aim is to propose effective basin management by enhancing the model so that it may suit PPCPs and estrogens. Thus, this chapter aims to compose a model and install reduction factors for building a model. Installing factors influences the change in PPCPs and estrogens and is an important element for an estimation model. This chapter considered 61 kinds of PPCPs and 4 kinds of estrogens by photolysis, biodegradation and adsorption at Gyeongan River. The final purpose of this chapter is to prepare the basis for building a model suitable for Gyeongan River. River water and soil sampled from Gyeongan River will be used for biodegradation and adsorption of PPCPs and estrogens, verification of reduction rate and building a model by sorting PPCPs and estrogens decomposed by the sunlight.

6.2 Methods

6.2.1 Pathway of PPCPs and estrogens

Since PPCPs are used diversely, their pathways of exposure to environment are also diverse and hard to predict (William. 2005). Figure 6.1 shows small and large STPs located on the Gyeongan River basin and the river map using GIS. There are 22 STPs whose treated wastewater is discharged into Gyeongan River. They treat wastewater with diverse processes such as membrane bioreactor (MBR), new biosorption system (NBS), sequencing batch reactor (SBR) and oxidation ditch method (as shown in Chapter V).

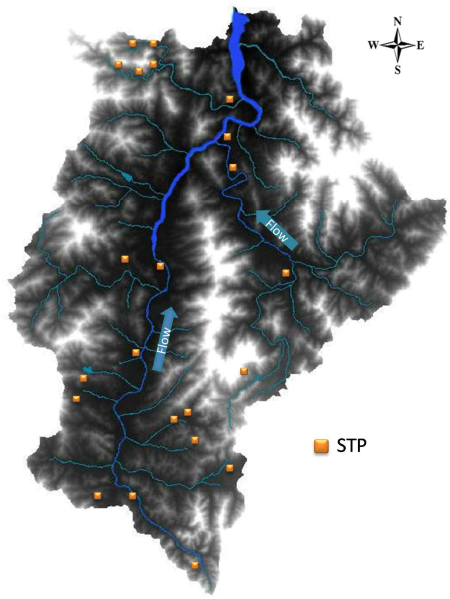

Figure 6.1 Location of large and small STPs on the Gyeongan River basin

6.2.2 Approach for model parameters

When PPCPs and estrogens are introduced into a river, we should consider the change of concentrations. While PPCPs and estrogens flowing along the river, they may be reduced in concentration, decomposed or adsorbed. In the daytime, the sun is consistently shining on the river, live in a variety of microorganisms and there is soil and sand on the riverbed to adsorb PPCPs and estrogens. To consider the change of PPCPs and estrogens, this study conducted experiments on photolysis, biodegradation and adsorption. Factor experiment needed for the model was conducted by dividing Gyeongan River into upstream, downstream and tributary with sampling points shown in Figure 6.2.

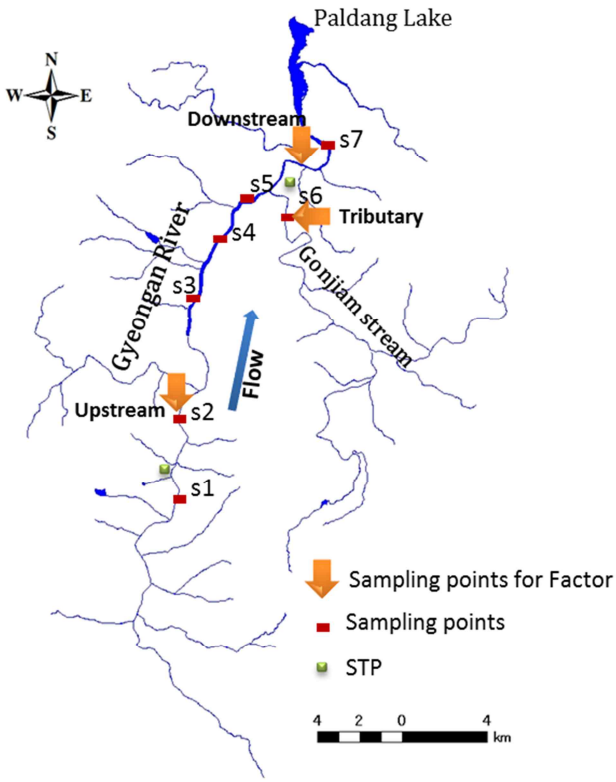

Figure 6.2 Sampling points for factor experiment

Sampling for factor experiment was carried out at s2 point for upstream, between s5 and s7 for downstream, and at s6 for tributary. Sampling of the river water was conducted at a place with the best flow, the same as the existing one, while river soil was collected by mixing the center and both sides of the river uniformly.

6.2.2.1 Photolysis

Photolysis was conducted in accordance with the US EPA (Environmental Protection Agency).

Equipment and conditions of the experiment are shown in Table 6.1 and Figure 6.3. With mixed standard solution (10 μg L^{-1}) added to quartz tube, it was exposed to solar light in right angles by tipping around 30° from vertical direction. Then, a control experiment in lightless condition was conducted to verify the change of PPCPs in a shield of the light. Equation 1 was used to calculate the constant of photolysis (Tixier, C. et al., 2002). This equation was derived from a mass balance approach on the assumption that the natural attenuation follows a first-order reaction. (Zepp, R. G. et al., 1977; Tixier, C. et al., 2002)

Table 6.1 Conditions of photolysis experiments

Day	1	2	3	4	5	6
Water temp.(℃)	15.0	14.0	14.1	11.3	14.7	17.7
Standard	10 μg/L					
Sample volume	10 mL					
Control	blocking light using aluminum foil and kept 24 hours					

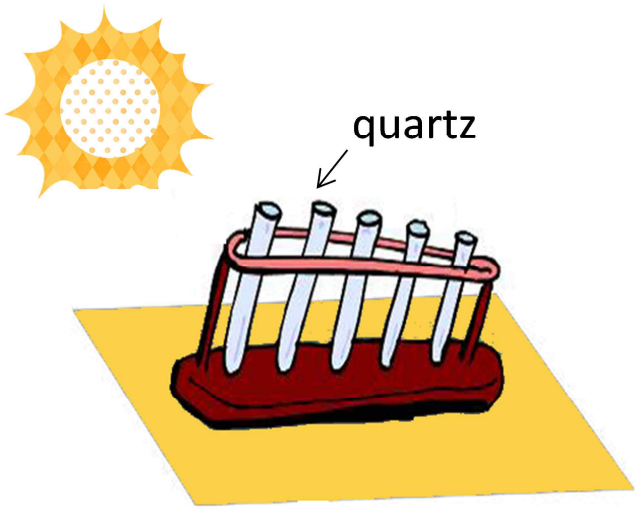

Figure 6.3 Equipment of photolysis (Hanmoto S. 2013)

$$k_{p_i} = \varphi \times \left\{ \frac{UVB_i \times \left(1 - R_{UVB\ i}\right) \times \left(1 - B_{UVB\ i}\right)}{UVB_t} \times \sum_{\lambda=297.5}^{315} \frac{L_\lambda \times \left(1 - 10^{-\alpha_{\lambda_i} \times l_i}\right) \times \varepsilon_\lambda}{\alpha_{\lambda_i} \times D_i} + \frac{UVA_i \times \left(1 - R_{UVA\ i}\right) \times (1 - B_{UVA\ i})}{UVA_t} \times \sum_{\lambda=315}^{490} \frac{L_\lambda \times \left(1 - 10^{-\alpha_{\lambda_i} \times l_i}\right) \times \varepsilon_\lambda}{\alpha_{\lambda_i} \times D_i} \right\} \quad eq\ 1$$

where φ is quantum yield of the PPCPs and estrogens (−), ε_λ is molar absorptivity, UVB_i and UVA_i are sunlight intensity at Earth's surface in those wavelengths (W/m^2), UVB_t and UVA_t are annual average sunlight intensity at Earth's surface in those wavelengths (W/m^2), $RUVB_i$ and $RUVA_i$ are fraction of sunlight reflected at the surface of the water body in those wavelengths (−), $BUVB_t$ and $BUVA_i$ are fraction of sunlight shaded by water plants in those wavelengths (−), UVB_t and UVA_t are annual average sunlight intensity at Earth's surface in those wavelengths (W/m^2), L_λ is annual average sunlight intensity at Earth's surface at wavelength λ (mmol cm^{-2} hr^{-1}), α_λ is decadic absorption coefficient of the water body at wavelength λ (m^{-1}), D_i is depth of the water (m), and l_i is path length of sunlight in the water (m). UVA and UVB were used the measurements of Seoul, the region nearest to the research site (37.56N, 126.93E; Yonsei University).

6.2.2.2 Biodegradation

Biodegradation experiment was conducted with the condition of Table 6.2 and Figure 6.4 (Lawrence A. et al., 2000) to understand decomposition of PPCPs and estrogens caused by diverse microorganisms at Gyeongan River. River water was sampled at upstream (s2) and downstream (s7) of Gyeongan River to move to the lab in room temperature. The samples were prepared in division into sterilized and unsterilized ones using autoclave. The experiment includes the influence of suspended solid (SS), container adsorption and hydrolysis on the change in concentrations of the target compounds. As the result, it was possible to know the exact amount of biodegradation by conducting an experiment in the same conditions on the sample in disinfection of the river water with autoclave (Hanmoto S. 2013). Each sample was put in the erlenmeyer flask adding standard substances with an initial concentration at 1 μg L-1. For experiment, after keeping 20 ℃ rotating stirring was conducted using vibrator in a shield of the light, collecting samples 0, 24, 48 and 72 hours later.

Table 6.2 Conditions of biodegradation experiments

Sample	Sterilize			Non sterilize	
	Milii-Q	Upstream	Downstream	Upstream	Downstream
pH	-	7.3	7.8	-	-
Water temp.	20 ℃				
Sample volume	150 mL				
Sampling time	0, 24, 48, 72 hr				
Centrifugation	100 rpm				
Standard	1 μg/L				

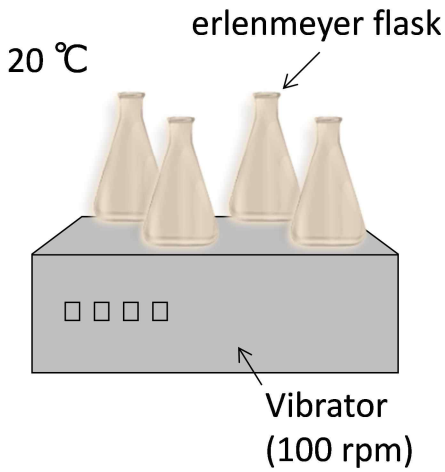

Figure 6.4 Equipment of biodegradation

$$k_b = k_{ns} - k_s \qquad eq2$$

k_b means rate constant of biodegradation (day^{-1}), k_{ns}, reaction rate constant for non-sterilization system, and k_s, for sterilization system. Using the Equation 2 above, it was understood how large amount of each PPCP and estrogen is decomposed at Gyeongan River by microorganisms.

6.2.2.3 Adsorption

Experiment of adsorption was conducted using the soil and sand collected from Gyeongan River with the condition shown in the following Table 6.3 and Fiugre 6.5 (OECD 2000). When sampling the soil and sand from the river, they were collected from the central point of the river and points of both sides to mix the same amount for use. Soil and sand were collected from the upstream (s2) and downstream (s7) of Gyeongan River to mix. Samples collected were dried in nature and then

used for experiment by filtering with a sieve of 2 mm. After sieving, only particles less than 2 mm that passed through the sieve were used for experiment. Before using for experiment, light was shielded at 25 °C and then equilibration was carried out by stirring it for over 12 hours. Then, experiment started by adding standard solution in mixture with PPCPs and estrogens at an initial concentration of 50 μg L^{-1}.

Table 6.3 Conditions of adsorption experiments

Day	Blank	Control	A	B	C	D	E	F
Standard (0.02 %)	-	3 mL						
Dry weight (g)	5	-	0.5	1	2	3	4	5
Solvent	Calcium chloride + Sodium azide							
pH	5.7	5.8	5.7	5.7	5.8	5.7	5.7	5.9

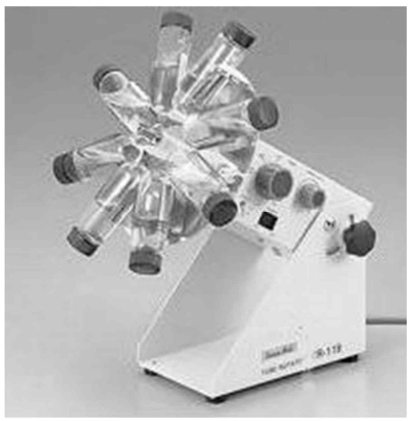

Figure 6.5 Equipment of adsorption

6.3 Results and discussion

6.3.1 Photolysis

6.3.1.1 UVA and UVB

How large the measures of UVA and UVB run to is important to consider photolysis. The results of UVA and UVB from Seoul were used as the nearest measuring place to the research site. Then, Figure 6.6 shows the results of UVA and UVB measured (Yonsei University).

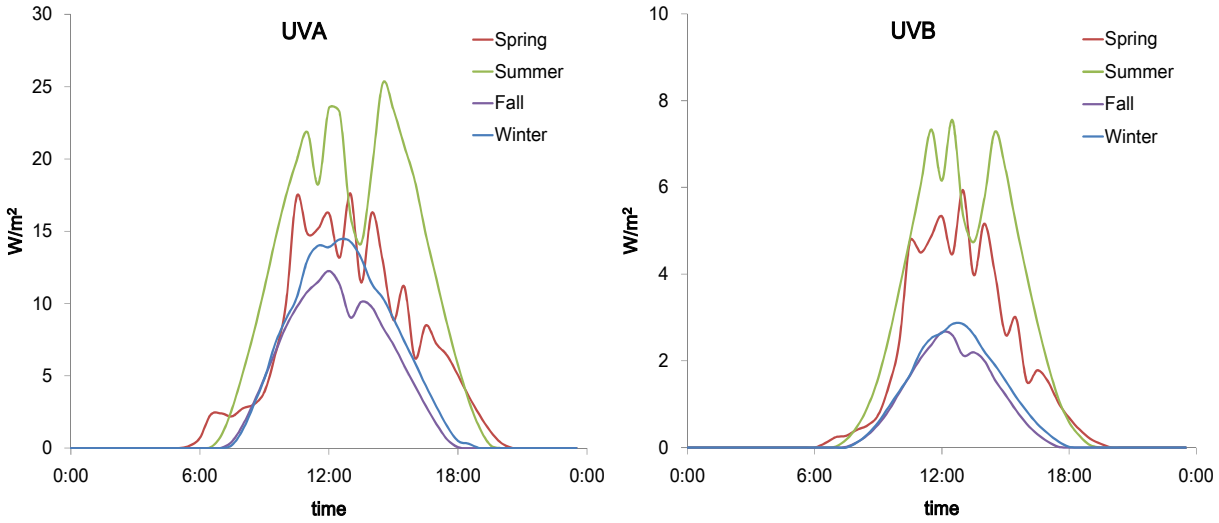

Figure 6.6 UVA and UVB measured at Seoul by monthly mean (2012~2013)

UVA and UVB showed the highest measures in spring and summer and both were measured at 0 from midnight to five in the morning and from 21th to 24th hour, respectively. That is, from 5th to 21st hour, UV seems to affect PPCPs and estrogens.

6.3.1.2 Photolysis of PPCPs and estrogens

This study included 61 compounds of PPCPs and 4 compounds of estrogens selected. Besides, photolysis was conducted on 28 compounds of PPCPs and estrogens selected for substances of high decaying ratios (over 10 %) by the sunshine (Figure 6.7) (Hanmoto S. 2013).

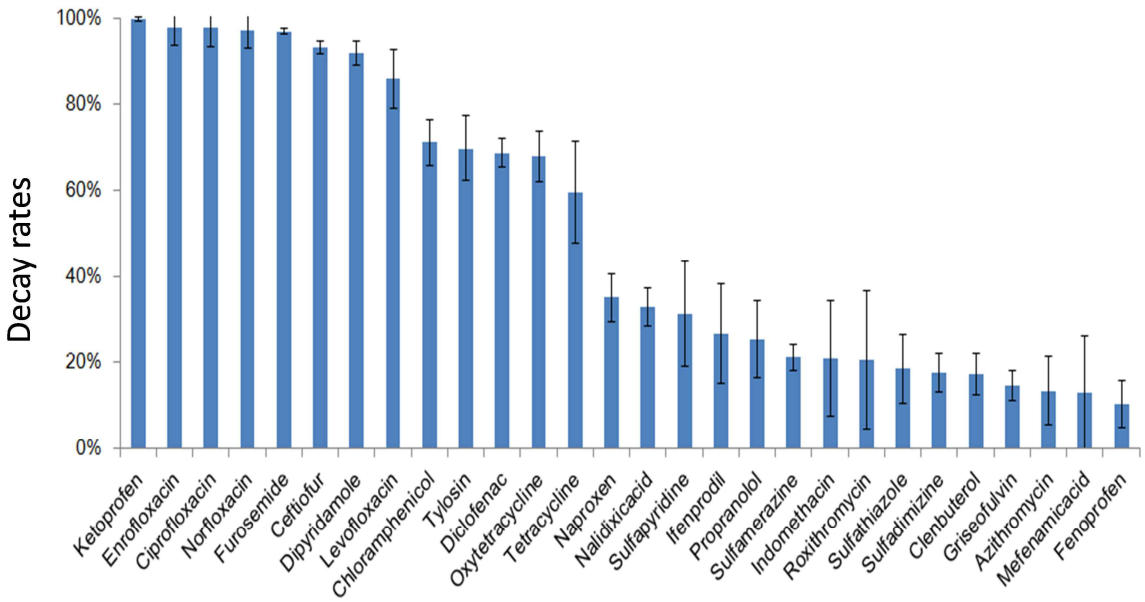

Figure 6.7 Decay rates of 28 materials showing a decay rate over 10 % (Hanamoto S. 2013)

Substances with a decaying ratio over 10% included NSAIDs such as diclofenac, fenoprofen, furosemide, indomethacin, ketoprofen, mefenamicacid, naproxen, and sulfapyridine. Antibiotics included azithromycin, ceftiofur, chloramphenicol, ciprofloxacin, enrofloxacin, levofloxacin, nalidixicacid, norfloxacin, oxytetracycline, roxithromycin, sulfadimizine, sulfamerazine, sulfathiazole, tetracycline and tylosin. The other PPCPs are cenbuterol, dipyridamole, griseofulvin, ifenprodil, and propranolol. For ελ (molar absorptivity), photometry was conducted at an interval of 0.5 nm in the span of 290 nm to 500 nm using spectrophotometer (UV-2500PC, Shimadzu, Kyoto, Japan) on the subject matters and estrogens selected through the rate constant experiment of photolysis by the sun's ray with the result shown in Figure 6.8 and Table 6.4 (Hanamoto S. 2013).

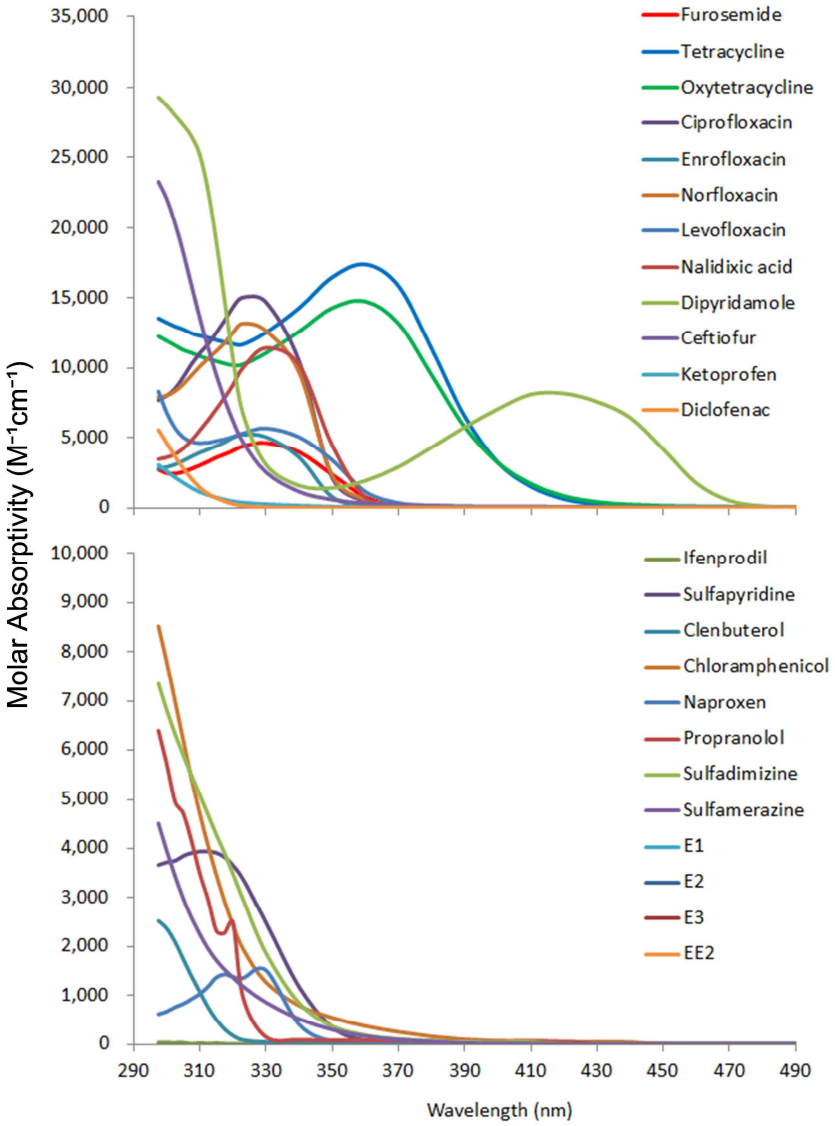

Figure 6.8 Molar absorption coefficients of PPCPs (Hanmoto S. 2013) and estrogens in selected 24 kinds

Table 6.4 Molar absorption coefficients of PPCPs (Hanmoto S. 2013) and estrogens

λ(nm)	ε (M-1cm-1)											
	Furosemide	Tetracycline	Oxytetracycline	Ciprofloxacin	Enrofloxacin	Norfloxacin	Levofloxacin	Nalidixic acid	Dipyridamole	Ceftiofur	Ketoprofen	Diclofenac
490	0	18	63	0	0	0	0	0	39	0	0	0
480	0	19	70	0	0	0	0	0	124	0	0	0
470	0	21	87	0	0	0	0	0	503	0	0	0
460	0	21	106	0	0	0	0	0	1749	0	0	0
450	0	46	146	0	0	0	0	0	4164	0	0	0
440	0	94	233	0	0	0	0	0	6434	0	0	0
430	0	243	416	0	0	0	0	0	7573	0	0	0
420	0	624	834	0	0	0	10	0	8168	81	0	0
410	0	1514	1709	0	0	0	12	0	8104	93	0	0
400	0	3231	3214	0	0	0	17	0	7054	91	0	0
390	0	6530	5772	0	0	8	55	0	5754	112	0	0
380	0	11390	9503	0	12	67	134	0	4300	167	0	0
370	109	15852	13188	56	68	200	341	45	2917	214	16	0
360	766	17385	14763	473	199	586	1143	723	1927	321	38	0
350	2361	16482	14287	2117	761	2274	3389	4441	1405	578	87	0
340	3969	14289	12617	10482	3592	9689	5040	10222	1573	1147	157	0
330	4623	12555	11080	14700	5047	12661	5675	11444	3058	2520	257	21
323.1	4384	11695	10262	15051	5208	13192	5319	10040	6661	4657	372	138
320	4065	11731	10205	14350	5000	12536	5055	8778	10676	6216	464	271
317.5	3807	11852	10317	13412	4672	11801	4893	7886	14803	7727	581	459
315	3583	12011	10491	12549	4403	11216	4770	7064	18987	9485	729	692
312.5	3290	12177	10641	11713	4162	10679	4638	6270	22630	11435	909	994
310	3023	12321	10851	11068	3932	10111	4611	5530	25183	13580	1122	1441
307.5	2780	12495	11085	10281	3653	9481	4710	4821	26487	15887	1419	2057
305	2565	12774	11291	9349	3352	8835	5030	4224	27307	18223	1780	2795
302.5	2434	12985	11622	8521	3077	8340	5685	3822	27990	20314	2166	3664
300	2468	13262	11950	8015	2898	8022	6801	3591	28698	22070	2598	4610
297.5	2725	13554	12275	7690	2792	7913	8314	3462	29285	23272	3051	5563
	Ifenprodil	Sulfapyridine	Clenbuterol	Chloramphenico	Naproxen	Propranolol	Sulfadimizine	Sulfamerazine	E1	E2	E3	EE2
490	0	0	0	0	0	0	0	0	3	6	0	0
480	0	0	0	0	0	0	0	0	4	6	0	0
470	0	0	0	0	0	0	0	0	4	6	0	0
460	0	0	0	0	0	0	0	0	4	7	0	0
450	0	0	0	0	0	0	0	0	4	7	0	0
440	0	0	0	44	0	0	0	0	4	7	0	0
430	0	0	0	48	0	0	0	0	5	8	0	0
420	0	0	0	53	31	49	0	0	5	8	0	0
410	0	0	0	62	30	60	46	12	5	9	0	0
400	0	0	0	66	0	54	42	11	6	10	0	0
390	0	0	0	97	0	57	48	21	6	10	0	1
380	0	0	0	160	33	65	69	53	6	11	0	0
370	4	20	0	251	38	73	106	95	7	12	0	1
360	0	73	33	371	38	79	186	163	7	12	0	0
350	7	345	27	542	55	82	369	298	8	14	0	1
340	11	1177	32	791	405	90	844	518	9	14	0	1
330	9	2491	45	1267	1513	147	1864	859	9	15	0	1
323.1	10	3375	85	1945	1359	949	2964	1182	10	17	0	1
320	6	3660	177	2442	1383	2497	3490	1368	10	17	0	1
317.5	11	3825	307	2924	1433	2280	3901	1528	11	17	0	1
315	19	3914	503	3464	1371	2323	4280	1719	11	18	0	1
312.5	14	3941	756	4054	1184	2960	4682	1955	11	18	0	1
310	23	3942	1075	4709	1032	3496	5087	2253	12	19	0	1
307.5	9	3911	1392	5417	925	4154	5483	2591	12	19	0	1
305	33	3851	1740	6200	829	4711	5900	2983	12	20	0	1
302.5	30	3754	2097	6996	761	4957	6334	3446	13	20	0	1
300	33	3721	2373	7797	670	5724	6816	3957	14	21	0	1
297.5	36	3669	2527	8522	618	6397	7354	4510	15	22	1	1

Molar absorptivity is the parameter indicating the absorbability of molecular photon. While the direct reaction of photolysis occurs in two stages of photonic absorption into molecules and reaction to decomposition, photolytic rate constant is calculated with the following Equation 3 using molar absorptivity and quantum yield.

$$k_p = \varphi \times \sum_{\lambda} \left(\varepsilon_{\lambda} \times L_{\lambda} \right) \qquad eq3$$

where k_p is direct photolysis rate constant (hr^{-1}), φ is quantum yield (-), ε_λ is molar absorption coefficient ($M^{-1}\ cm^{-1}$), L_λ is sunlight intensity (mmol $cm^{-2}\ hr^{-1}$).

EPA was referred to for L_λ, of which the value was used at latitude 40° N because of Seoul, Korea, being 37° N, and it was put in Table 6.5 (EPA 1998).

Table 6.5 L_λ Values for latitude 40° N.

λcenter (nm)	Spring	Summer	Fall	Winter
490	4.2E-01	4.9E-01	2.6E-01	1.7E-01
480	4.4E-01	5.1E-01	2.7E-01	1.7E-01
470	4.3E-01	5.0E-01	2.6E-01	1.7E-01
460	4.2E-01	4.9E-01	2.5E-01	1.6E-01
450	4.1E-01	4.8E-01	2.5E-01	1.6E-01
440	3.7E-01	4.3E-01	2.2E-01	1.4E-01
430	3.1E-01	3.6E-01	1.9E-01	1.2E-01
420	3.2E-01	3.7E-01	1.9E-01	1.2E-01
410	3.1E-01	3.6E-01	1.9E-01	1.2E-01
400	2.4E-01	2.8E-01	1.4E-01	9.1E-02
390	1.6E-01	1.9E-01	9.9E-02	6.3E-02
380	1.7E-01	2.0E-01	1.1E-01	6.8E-02
370	1.6E-01	1.9E-01	9.8E-02	6.2E-02
360	1.5E-01	1.8E-01	9.0E-02	5.7E-02
350	1.4E-01	1.6E-01	8.0E-02	5.0E-02
340	1.2E-01	1.5E-01	7.1E-02	4.3E-02
330	9.6E-02	1.2E-01	5.4E-02	3.2E-02
323.1	2.7E-02	3.4E-02	1.5E-02	8.3E-03
320	1.5E-02	1.9E-02	8.2E-03	4.2E-03
317.5	1.2E-02	1.6E-02	6.6E-03	3.2E-03
315	9.2E-02	1.2E-02	5.0E-03	2.2E-03
312.5	6.5E-03	9.1E-03	3.5E-03	1.4E-03
310	4.2E-03	6.2E-03	2.2E-03	7.5E-04
307.5	2.3E-03	3.7E-03	1.2E-03	3.4E-04
305	1.1E-03	2.0E-03	5.4E-04	1.2E-04
302.5	4.0E-04	8.3E-04	1.9E-04	3.0E-05
300	1.1E-04	2.7E-04	4.8E-05	5.1E-06
297.5	1.9E-05	6.2E-05	7.8E-06	5.5E-07

φ (quantum yield) for calculating Equation 1 was used in reference to related theses and put in Table 6.6 (Cunningham VL et al., 2008; . Hanamoto S. 2013)

Table 6.6 Quantum yield [-]

	φ[-]		
	μ	±	σ
	(min	-	max)
Ketoprofen	0.651931	-	0.692558
Enrofloxacin	0.052131	-	0.061074
Norfloxacin	0.009163	-	0.009438
Ciprofloxacin	0.008203	±	0.001134
Furosemide	0.013155	±	0.000972
Dipyridamole	0.000744	-	0.000752
Ceftiofur	0.013534	±	0.000912
Ofloxacin	0.005283	±	0.000323
Diclofenac	0.211108	±	0.011617
Oxytetracycline	0.000527	±	0.000105
Tylosin	-		-
Chloramphenicol	0.009409	±	0.000947
Tetracycline	0.000413	±	9.28E-05
Sulfapyridine	0.00471	±	0.000307
Naproxen	0.009014	±	0.000389
Ifenprodil	0.716872	±	0.083227
Propranolol	0.008673	±	0.000759
Indomethacin	-		-
Nalidixicacid	0.000592	±	4.64E-05
Sulfathiazole	-		-
Sulfamerazine	0.004346	±	0.000428
Sulfadimizine	0.001949	±	0.00035
Clenbuterol	0.034781	-	0.035762
Azithromycin	-		-
Griseofulvin	-		-
Mefenamicacid	-		-
Fenoprofen	-		-
Salbutamol	-		-
E1	0.0019		-
E2	0.00165		-
E3	0.0017		-
EE2	0.0015		-

Besides, for D_i (depth of the water), following the result of the values in MOE 2010 research report, mean depth of water 0.24 m was used from s1 to s5, 0.25 m for s6, and 0.4 m for s7. For path length of sunlight in the water (l_i), 1.2 times of water depth was used for the standard value of the light's transmitted distance in water (Zepp, R. G. 1977). Equation 1 is the expression in application of survey data to the above expression (Hanamoto S. 2013; Zepp. R. G. et al., 1977; Tixier C.et al., 2002), which is shown in Table 6.7 by calculating constant of photolysis. This model will consider the seasonal change by calculating reduction factors by season. So constants of photolysis were calculated by season and then for each of upstream, downstream and tributary.

Table 6.7 A constant of photolysis of PPCPs and estrogens

k_{pl} (hr^{-1})

	Upstream	Tributary	Downstream	Upstream	Tributary	Downstream	Upstream	Tributary	Downstream	Upstream	Tributary	Downstream	Upstream	Tributary	Downstream	Upstream	Tributary	Downstream	Upstream	Tributary	Downstream	Upstream	Tributary	Downstream
	Ketoprofen			**Enrofloxacin**			**Norfloxacin**			**Ciprofloxacin**			**Furosemide**			**Dipyridamole**			**Ceftiofur**			**Ofloxacin**		
Spring	0.87	0.84	0.52	0.88	0.84	0.53	0.40	0.39	0.24	0.40	0.38	0.24	0.27	0.26	0.17	0.38	0.36	0.24	0.22	0.21	0.13	0.01	0.01	0.00
Summer	1.28	1.23	0.77	1.18	1.13	0.71	0.54	0.52	0.33	0.54	0.52	0.32	0.37	0.36	0.22	0.50	0.49	0.32	0.32	0.31	0.19	0.01	0.01	0.01
Fall	0.42	0.41	0.25	0.44	0.42	0.26	0.20	0.19	0.12	0.20	0.19	0.12	0.13	0.12	0.08	0.11	0.11	0.07	0.10	0.10	0.06	0.00	0.00	0.00
Winter	0.33	0.32	0.20	0.32	0.31	0.19	0.15	0.14	0.09	0.15	0.14	0.09	0.09	0.09	0.06	0.08	0.08	0.05	0.08	0.08	0.05	0.00	0.00	0.00
	Diclofenac			**Oxytetracycline**			**Tylosin**			**Chloramphenicol**			**Tetracycline**			**Sulfapyridine**			**Naproxen**			**Ifenprodil**		
Spring	0.16	0.15	0.10	0.13	0.12	0.08	0.00	0.00	0.00	0.10	0.10	0.06	0.11	0.10	0.07	0.04	0.04	0.02	0.04	0.04	0.02	3.77	3.62	2.26
Summer	0.31	0.30	0.19	0.17	0.16	0.11	0.00	0.00	0.00	0.14	0.13	0.08	0.14	0.14	0.09	0.05	0.05	0.03	0.05	0.05	0.03	7.95	7.63	4.77
Fall	0.06	0.05	0.03	0.05	0.05	0.03	0.00	0.00	0.00	0.04	0.04	0.03	0.04	0.04	0.02	0.02	0.02	0.01	0.02	0.02	0.01	0.02	0.02	0.01
Winter	0.05	0.05	0.03	0.03	0.03	0.02	0.00	0.00	0.00	0.03	0.03	0.02	0.03	0.00	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
	Propranolol			**Indomethacin**			**Nalidixicacid**			**Sulfathiazole**			**Sulfamerazine**			**Sulfadimizine**			**Clenbuterol**			**Azithromycin**		
Spring	0.06	0.05	0.03	0.00	0.00	0.00	0.03	0.03	0.02	0.00	0.00	0.00	0.02	0.02	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.00
Summer	0.09	0.09	0.06	0.00	0.00	0.00	0.04	0.04	0.02	0.00	0.00	0.00	0.03	0.03	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.00	0.00	0.00
Fall	0.02	0.02	0.01	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.00	0.00	0.00
Winter	0.01	0.01	0.01	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.01	0.01	0.00	0.01	0.01	0.00	0.01	0.01	0.00	0.00	0.00	0.00
	Griseofulvin			**Mefenamicacid**			**Fenoprofen**			**Salbutamol**			**E1**			**E2**			**E3**			**EE2**		
Spring	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Summer	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fall	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Winter	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

6.3.2 Biodegradation

Experiment was conducted to verify the biolytic rate of PPCPs and estrogens at the upstream and downstream of Gyeongan River. Biodegradation of PPCPs and estrogens in the upstream and downstream results are shown in Table 6.8.

Table 6.8 Biodegradation rate (day^{-1})

		Biodegradation rate (day^{-1})	
		Upstream	Downstream
No.	Compound	μ	μ
1	2-QCA	0.012	0.090
2	Acetaminophen	-	-
3	Antipyrine	0.037	0.056
4	Atenolol	0.025	0.035
5	Bezafibrate	0.070	0.153
6	Caffeine	0.053	0.070
7	Carbamazepine	0.006	0.038
8	Ceftiofur	0.045	-
9	Clarithromycin	-	0.101
10	Clenbuterol	0.042	0.078
11	Clofibric_acid	0.013	0.017
12	Crotamiton	-	0.044
13	Cyclophosphamide	-	0.042
14	DEET	-	0.006
15	Diltiazem	0.014	0.095
16	Dipyridamole	0.360	0.651
17	Disopyramide	0.050	0.125
18	E1	-	0.004
19	E2	-	-
20	E3	0.024	0.026
21	Erythromycin	0.003	0.102
22	Erythromycin-HO	0.017	0.076
23	Ethenzamide	-	0.032
24	Fenoprofen	0.063	0.013
25	Furosemide	-	0.017
26	Griseofulvin	0.007	0.100
27	Ibuprofen	0.310	0.280
28	Ifenprodil	0.060	0.146
29	Isopropylantipyrine	0.021	0.034
30	Ketoprofen	0.001	0.044
31	Lincomycin	-	0.053
32	Mefenamic_acid	0.156	0.071
33	Metoprolol	-	-
34	Pirenzepine	-	0.045
35	Primidone	0.052	0.063
36	Propranolol	0.040	0.109
37	Roxithromycin	0.009	0.118
38	Salbutamol	0.010	0.033
39	Sulfadimethoxine	0.027	0.075
40	Sulfadimidine	-	0.058
41	Sulfamerazine	0.022	0.072
42	Sulfamethoxazole	0.002	0.071
43	Sulfamonomethoxine	0.013	0.036
44	Sulfapyridine	-	0.070
45	Sulfathiazole	-	0.074
46	Sulpiride	-	0.051
47	Theophylline	0.033	0.045
48	Tiamulin	0.076	0.061
49	Triclocarban	0.147	0.036
50	Trimethoprim	-	0.058
51	Tylosin	0.004	0.087

At the upstream of Gyeongan River appeared the decrease of dipyridamole, ibuprofen, bezafibrate, mefenamic acid and triclocarban caused by microorganisms while at the downstream appeared high biolytic rates of dipyridamole, ibuprofen, bezefibrate, ifenprodil, disopyramide,

roxithromycin, propranolol, erythromycin, clarithromycin, griseofulvin and diltiazem. At the upstream, biodegradation of PPCPs and estrogens were low while it is found to be generally high at the downstream (Figure 6.9).

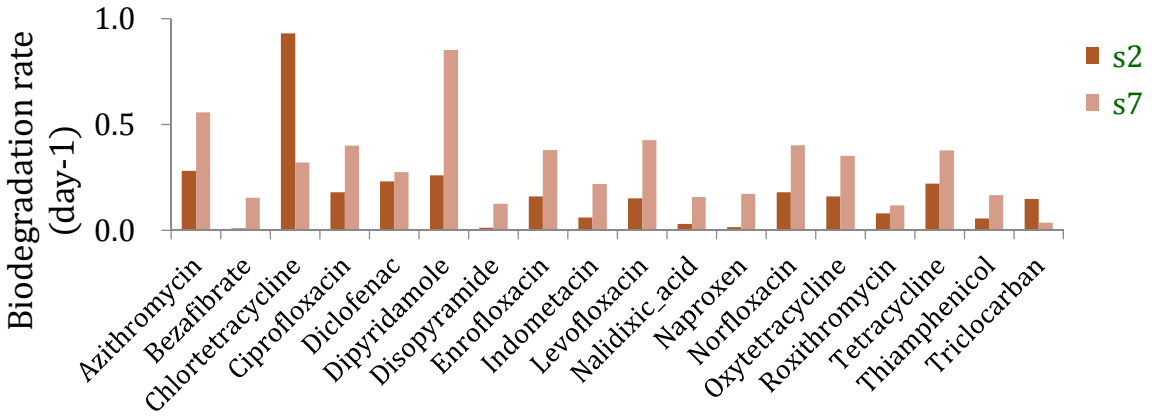

Figure 6.9 Comparison of biodegradation rate in upper and lower Gyeongan River

Using the above results of experiment, substances were divided into those likely and unlikely to be influenced by biodegradation. Though Gyeongan River 49.3 km long has a great variation in the time of flow by season, decay rate was calculated by putting time of flow at 1 day (MOE. 2010).

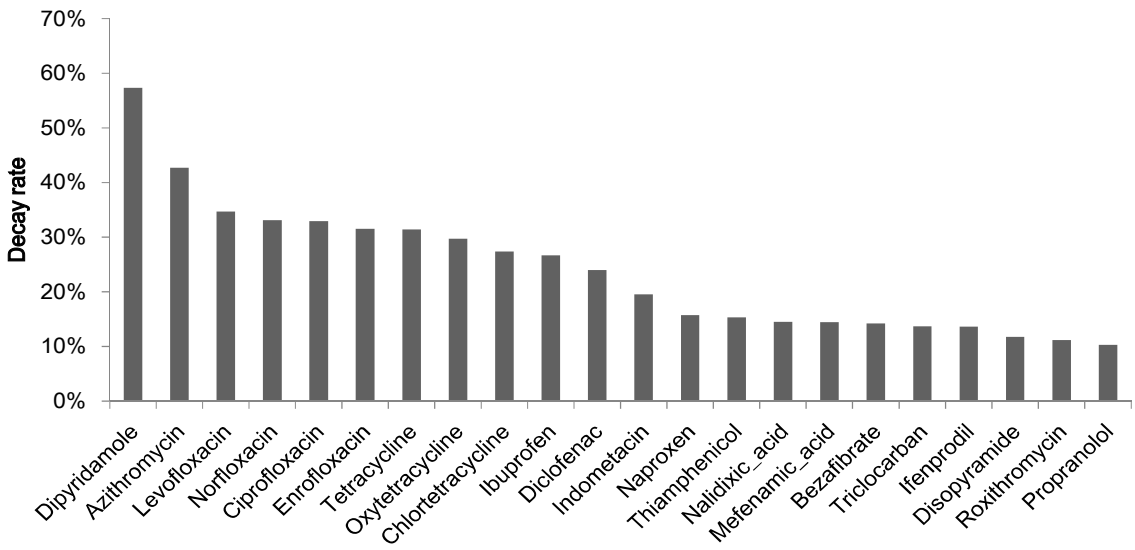

Figure 6.10 22 substances showing the decay rate over 10%

22 substances with a decay rate over 10 % were selected as those influenced by biodegradation while those under 10 % were regarded as unlikely to be.

6.3.3 Adsorption

Based on the experiment method of 6.2.2.3, experiments on adsorption of PPCPs and estrogens were conducted with the result shown in Table 6.9. In the control sample for observation of change after the injection of only standard substances, those with decay rate over 10 % included sulpiride, pirenzepine, nalidixic acid, diltiazem, bezafibrate, fenoprofen, diclofenac, indomethacin, triclosan, chlortetracycline, erythromycin-H2O, and triclocarban. These substances considered to have decreased in the ratio for reasons of hydrolysis, adsorption to container were excluded from the experiment of adsorption. It is our knowledge that matters with solid/liquid partition coefficients under 1.5, as shown in Table 6.9, can be hardly influenced by adsorption (Hanamoto S. 2013). Though there are substances over 1.5, this experiment applied a model excluding adsorption. Because, there are limitations in this experiment: Since it was the verification of adsorption by in-vitro stirring with a simple revolution where there was no water flow, it is not certain whether this is actually adsorbed in the river. Besides, since there are diverse particles and substances in the river, we cannot exactly say that PPCPs and estrogens are adsorbed as the adsorption experiment above.

Table 6.9 Solide/liquid partition coefficients of adsorption

Solid/liquid partition coefficients (Kd, L/kg)							
No.	Compounds	average	SD (±)	No.	Compounds	average	SD (±)
1	Acetaminophen	1.4	0.2	28	Metoprolol	1.9	0.2
2	Antipyrine	1.1	0.3	29	Naproxen	2.2	0.2
3	Atenolol	3.9	0.2	30	Norfloxacin	1.2	0.1
4	Azithromycin	6.5	0.1	31	Oxytetracycline	7.2	0.5
5	Caffeine	0.5	0.0	32	Primidone	1.2	0.1
6	Carbamazepine	0.5	0.1	33	Propranolol	0.3	0.2
7	Ceftiofur	1.3	0.4	34	2-QCA	1.6	0.1
8	Chloramphenicol	3.1	0.2	35	Roxithromycin	2.0	0.2
9	Ciprofloxacin	7.5	0.5	36	Salbutamol	2.0	0.3
10	Clarithromycin	0.3	0.1	37	Sulfadimethoxine	2.6	0.2
11	Clenbuterol	0.9	0.1	38	Sulfadimidine	2.2	0.1
12	Clofibric_acid	1.2	0.2	39	Sulfamerazine	0.4	0.0
13	Crotamiton	1.4	0.1	40	Sulfamethoxazole	0.9	0.3
14	Cyclophosphamide	1.7	0.3	41	Sulfamonomethoxine	3.2	1.0
15	DEET	0.7	0.1	42	Sulfapyridine	0.5	0.1
16	Dipyridamole	1.9	0.2	43	Sulfathiazole	0.7	0.0
17	Disopyramide	1.4	0.1	44	Tetracycline	8.7	0.4
18	Enrofloxacin	3.0	0.3	45	Theophylline	0.3	0.1
19	Ethenzamide	0.9	0.1	46	Thiamphenicol	1.9	0.2
20	Furosemide	0.6	0.1	47	Tiamulin	0.6	0.1
21	Griseofulvin	2.4	0.3	48	Trimethoprim	0.9	0.1
22	Ibuprofen	0.7	0.0	49	Tylosin	1.0	0.3
23	Ifenprodil	0.1	0.0	50	E1	1.4	0.2
24	Isopropylantipyrine	1.5	0.1	51	E2	1.9	0.2
25	Ketoprofen	2.6	0.3	52	E3	1.6	0.1
26	Levofloxacin	1.9	0.1	53	EE2	0.1	0.0
27	Mefenamic_acid	2.2	0.2				

6.4 Conclusions

PPCPs and estrogens introduced into the river through diverse pathways flow to the downstream with the river. While moving along the river, PPCPs and estrogens are influenced by photolysis, biodegradation and adsorption. To install the factors of model, this study conducted experiments of photolysis, biodegradation and adsorption on the Gyeongan River.

1) In photolytic experiment, a total of 28 substances, including 8 substances of NSAIDs, 15 of Antibiotics and the other 5, showed a decay rate over 10%. Through photolytic experiment, it was possible to know the photolysis constant of 28 PPCPs and 4 estrogens by season for upstream, downstream and tributary.

2) Biodegradation was conducted in division into upstream and downstream and the latter showed higher decay rates. PPCPs and estrogens with a decay rate over 10 % were sorted into 22 compounds. At the upstream of Gyeongan River appeared the decrease of ibuprofen, mefenamic acid and triclocarban caused by microorganisms while at the downstream appeared high biolytic rates of dipyridamole, azithromycin, levofloxacin, norfloxacin, ciprofloxacin, enrofloxacin, tetracycline and oxytetracycline. At the upstream, biodegradation of PPCPs and estrogens were low while it is found to be generally high at the downstream. Other substances were under 10 % of decay rate, which was considered to have a low contribution to biodegradation.

3) Lastly, since adsorption mostly showed a low decay rate, this study concluded that there is no change of PPCPs and estrogens studied caused by adsorption. Because this experiment: Since it was the verification of adsorption by in-vitro stirring with a simple revolution where there was no water flow, it is not certain whether this is actually adsorbed in the river. Besides, since there are diverse particles and substances in the river, we cannot exactly say that PPCPs and estrogens are adsorbed as the adsorption experiment above.

This produced reducing factors of PPCPs and estrogens needed in building a river basin management model suited for Gyeongan River. Using the produced factors, this study is going to apply a model to Gyeongan River in Chapter VII.

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CHAPTER VII

RISK EVALUATION AND PREDICTIVE MODEL FOR WATERSHED MANAGEMENT IN THE GYEONGAN RIVER

7.1 Introduction

For Gyeongan River influent to Paldang Lake, which is used for drinking water, there are many reported studies related to contamination (Lee H.G. et al., 2007; Na Y.H. et al., 2005), but hardly any reports on the occurrence and management of substances such as pharmaceuticals and personal care products (PPCPs), Veterinary pharmaceuticals (VPs) and estrogens. One of the reasons to choose Gyeongan River for the target is that there is a sewage treatment plants (STPs) treating livestock wastewater with domestic wastewater. On the Gyeongan River basin, which is an important drinking water source, there are many STPs including one which treats livestock wastewater (MOE. 2012).

As mentioned in Chapter III and IV, PPCPs, VPs and estrogens are being introduced to STP while PPCPs, VPs and estrogens remaining in the treatment process are introduced to the river (Chapter V). To build a model suited for Gyeongan River, water and soil of the river were sampled to produce reducing factors through the experiments of photolysis and biodegradation (Chapter VI). Model for exact prediction of PPCPs and estrogens in Gyeongan River were constructed in Chapter VII with many factors and it was applied on Gyeongan River. Generally, for estimating the PPCPs appearing at STP, there are many studies based on the usage of pharmaceuticals. This is followed by the assumption that the total amount in the human body excluding the loss is introduced to STPs (Park J.I. et al., 2010). Estimation based on the amount of loss from the human body has limitations: It is impossible to know the loss of numerous chemicals from the human body with very few reported studies.

However, this study estimated the production of PPCPs and estrogens at STP based on pharmaceuticals detected from the influent of STP surveyed from 2011 through 2014. Then, using factors calculated in Chapter VI, concentrations of PPCPs and estrogens estimated in the river were calculated to compare with surveyed concentrations for evaluating definitude and restriction of the model. It also aims to propose a method to manage Gyeongan River effectively and minimize the contamination of Paldang Lake.

7.2 Methods

7.2.1 Model constitution

Gyeongan River with the main inflow of PPCPs and estrogens are the STPs, which is the most

important source of pollution. Figure 7.1 shows the inflow of PPCPs and estrogens at Gyeongan River and components of modeling.

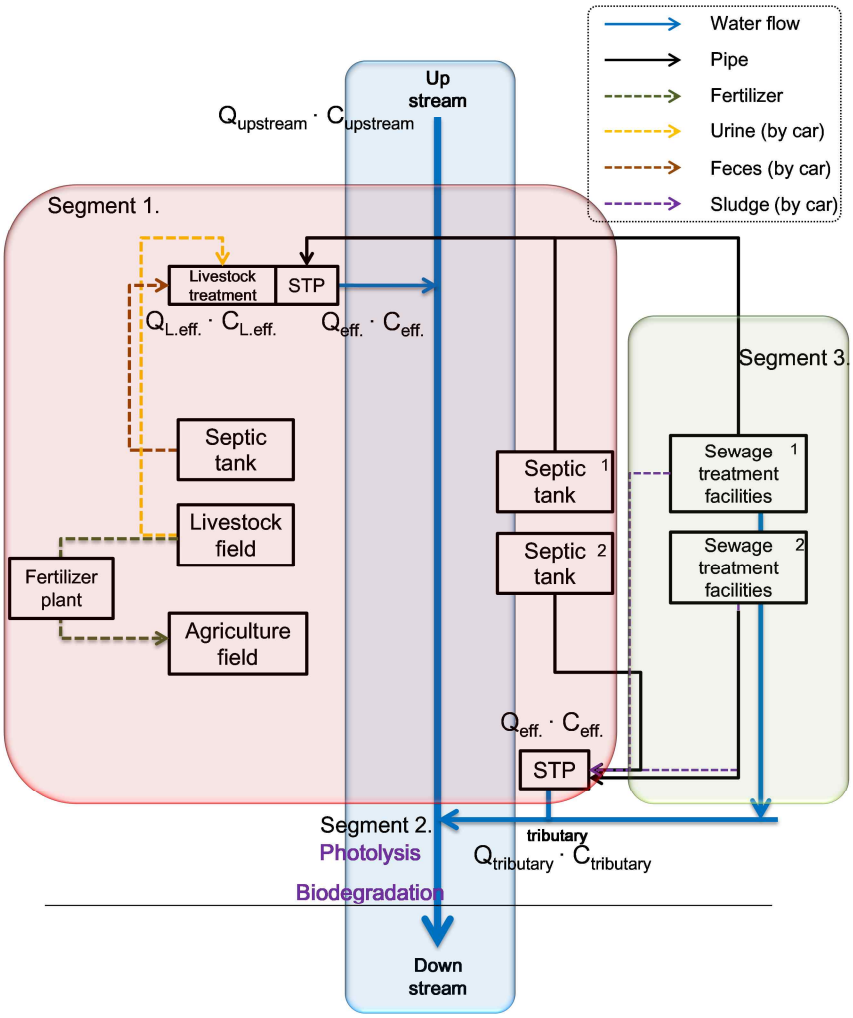

Figure 7.1 Division of cases by modeling components and inflow possibility

Modeling largely consists of three segments. The first segment is the inflow of residual PPCPs and estrogens into the river without being treated at the STPs. The STP is the most important source of pollution because PPCPs and estrogens exist in great quantities in domestic wastewater. PPCPs and estrogens existing in the execrations and wastewater from humans or animals are mostly being introduced into the STPs. The second segment is the contamination of river. PPCPs and estrogens flowing along the river, they may be reduced in concentration, decomposed or photolysis. The last segment is PPCPs and estrogens flowed in the river from sewage treatment facilities (Chapter V).

7.2.1 Modeling of predicted concentration of effluent in STPs

For concentration of PPCPs and estrogens at the river, calculation were made based on the concentration of PPCPs and estrogens detected from the influent of STPs. Using the concentration

of PPCPs and estrogens introduced for 3 years from two STPs representing the Gyeongan River basin, possible volumes of generation in one person were calculated for use. Generally, this result gives more accurate inflow of PPCPs and estrogens than the data based on the use of PPCPs. Volume of PPCPs and estrogens flowed into STPs (M_{STP}, mg/day.person) were calculated using the following expression.

$$M_{STP} = \frac{Q_{Inf} \times C_{Inf} \times (100\,\% - R_{STP})}{P} \qquad eq\,1$$

where P is population served by a given treatment plant, Q_{Inf} is flow rate of the influent (m^3/day), C_{Inf} is the concentration of PPCPs and estrogens in the influent (ng/L), R_{STP} is the removal efficiency in STP (%).

7.2.2 Prediction of concentration in the river

The following expression was used to predict the concentration of PPCPs and estrogens introduced in the river (PAUL D. A. et al., 2004).

$$C_{PEC} = \frac{[(M_o e^{-kt_R}) + \sum(M_i e^{-kt_i})]}{Q} \qquad eq\,2$$

C_{PEC} is predicted environmental concentration of the compound (mg/L), M_o is mass loading from upstream (g/day), k is decay rate constant (day^{-1}), t_R is travel time (day), M_i is mass loading of PPCPs and estrogens from the STPs (g/day), t_i is travel time from the STPs (day), and Q is flow rate (m^3/day). This is the model in which the change of compounds can be considered as PPCPs and estrogens introduced in the river moves with the river. So this study enabled decay rate *k* to predict the accurate concentration of each of PPCPs and estrogens by using the known results from experiments of photolysis, biodegradation and adsorption (Chapter VI).

7.3 Results and discussion

7.3.1 Modeling

7.3.1.1 Predicted concentration of effluent of STPs

Using Equation 1, PPCPs and estrogens inflowed in Gyeongan River were predicted from effluents of the STPs E and F. Of STPs at Gyeongan River, concentration of PPCPs and estrogens in effluent were predicted for two plants which give the biggest influence on the area of research (Figure 7.2).

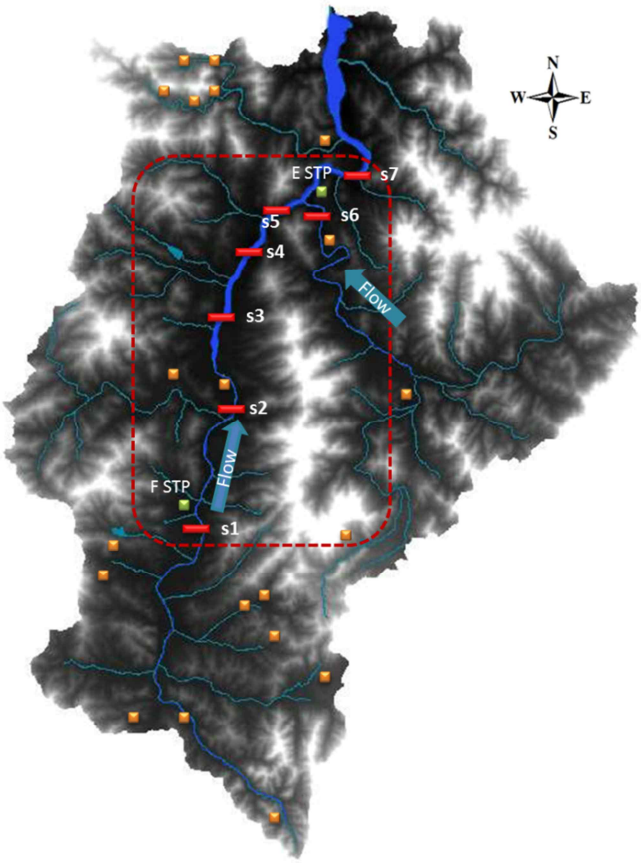

Figure 7.2 Locations of the river and STPs in the modeling area

By selecting point s1 to s7 at Gyeongan River as the target area for modeling, concentrations of PPCPs and estrogens were estimated in consideration of the generation of STPs E and F. Treating population for STP-E is 70,959 and STP-F is 109,300 while wastewater generation is around 40,000 m^3/day for STP-F and around 25,000 m^3 for STP-E (KNSO. 2013). Using the result of survey for 3 years at STPs E and F, average removal efficiency by season were shown in Table 7.1. This Table shows the removal efficiency of PPCPs and estrogens by season using concentrations measured at STPs from 2011 through 2014 (Chapter III).

Table 7.1 Removal efficiency of PPCPs and estrogen by season at STPs E and F

	Removal efficiency (%)							
	STP E				STP F			
	Spring	Summer	Fall	Winter	Spring	Summer	Fall	Winter
Acetaminophen	99.9	100.0	100.0	99.8	100.0	100.0	100.0	99.9
Caffeine	99.5	99.1	99.3	99.6	99.5	98.4	98.1	99.5
Ibuprofen	99.9	97.1	99.9	98.5	99.7	99.4	99.4	98.9
Naproxen	96.7	92.6	93.1	82.1	95.8	91.3	95.4	87.8
Theophylline	97.4	92.9	98.2	98.7	99.0	97.2	97.5	98.3
Ciprofloxacin	92.6	89.6	89.7	78.7	86.9	98.4	59.8	94.5
Sulpiride	2.6	48.8	22.9	26.0	55.0	59.2	54.2	12.8
Levofloxacin	73.3	65.1	74.6	64.4	72.2	95.4	91.6	93.2
DEET	21.9	28.4	48.7	8.3	-	-	3.2	-
Clarithromycin	36.0	55.5	51.9	19.9	40.6	52.8	55.0	23.3
Bezafibrate	93.1	94.7	65.5	-	82.1	85.9	41.9	22.1
Atenolol	53.0	43.1	49.0	35.6	90.4	92.9	85.7	77.1
Mefenamic_acid	51.9	34.5	34.0	35.1	59.8	65.3	58.1	39.8
Sulfamethoxazole	-	-	3.0	12.1	71.3	48.5	45.1	57.3
Ketoprofen	95.5	76.2	96.2	85.4	72.2	63.7	45.7	43.9
Roxithromycin	28.3	44.3	13.1	23.3	36.7	32.9	15.4	19.0
Furosemide	83.4	67.8	73.8	46.2	62.8	63.3	28.7	60.1
Sulfapyridine	-	-	-	13.6	-	55.4	28.0	47.2
Triclosan	94.4	100.0	89.5	100.0	72.6	-	-	-
Trimethoprim	8.1	52.5	47.4	-	60.8	39.8	41.9	0.8
Crotamiton	2.7	-	-	-	31.2	-	-	-
Carbamazepine	-	-	-	-	18.4	25.0	3.7	6.2
Triclocarban	79.3	56.5	41.2	79.6	56.8	22.1	65.5	30.5
Azithromycin	-	68.9	4.3	2.8	-	-	2.9	17.7
Oxytetracycline	98.9	100.0	90.6	96.7	100.0	97.3	-	97.8
Lincomycin	52.2	41.7	-	-	34.0	25.2	-	24.3
Diclofenac	-	40.8	-	-	9.0	-	-	-
Sulfadimidine	46.5	21.9	36.7	53.8	15.9	37.3	-	8.5
Estriol	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Enrofloxacin	68.9	-	92.0	70.2	69.5	-	-	96.3
Norfloxacin	88.8	87.3	87.5	39.5	94.9	100.0	100.0	-
Diltiazem	34.1	57.5	39.4	39.5	55.9	62.5	59.6	38.7
Tetracycline	97.4	93.6	98.5	86.1	99.1	100.0	100.0	98.4
Erythromycin	47.8	-	34.0	20.9	69.7	-	100.0	100.0
Erythromycin-H2O	4.0	74.0	13.3	23.6	27.5	37.4	27.7	56.9
Propranolol	-	-	-	-	36.9	14.3	-	-
Fenoprofen	100.0	-	100.0	94.0	100.0	-	100.0	91.4
Chlortetracycline	-	-	-	-	92.7	100.0	100.0	87.1
Estrone	97.6	96.1	92.6	92.5	92.3	85.4	82.8	90.8
Antipyrine	-	28.1	-	-	9.0	20.3	-	8.0
Tiamulin	-	-	-	-	-	-	-	4.1
Indometacin	36.6	83.7	31.4	0.0	37.0	15.6	-	-
Estradiol	100.0	100.0	100.0	100.0	100.0	-	100.0	-
Primidone	-	-	-	2.8	-	28.4	63.1	76.1
Salbutamol	-	-	-	-	-	-	-	100.0
Metoprolol	59.4	-	-	29.4	26.0	23.9	17.4	42.3
Griseofulvin	58.0	-	-	43.7	35.0	-	-	-
Ethenzamide	-	-	-	-	-	-	-	-
Tylosin	-	-	-	-	-	78.7	20.0	10.6
2QCA	-	-	-	-	29.7	-	-	-
Isopropylantipyrine	-	-	-	6.2	-	-	-	-
Sulfadimethoxine	-	-	-	-	-	34.2	58.6	48.3
Pirenzepine	-	-	-	-	-	-	-	-
Disopyramide	-	-	-	-	-	-	-	-
Dipyridamole	-	-	-	-	-	-	-	-
Clofibric_acid	-	-	-	-	-	-	29.1	-
Sulfathiazole	-	-	-	-	7.7	54.0	20.5	46.9
Sulfamerazine	-	-	-	-	-	-	-	-
Nalidixic_acid	-	-	-	-	-	-	-	-
Sulfamonomethoxine	-	-	-	-	-	-	-	-
Ceftiofur	-	-	-	-	-	-	-	-
Clenbuterol	-	-	-	-	-	-	-	-
Ifenprodil	-	-	-	-	-	-	-	-
Thiamphenicol	-	-	-	-	-	-	-	33.3
Ethynylestradiol	-	-	-	-	-	-	-	-

Q_{in} and C_{in} for the calculation of Equation 1 used the concentrations and inflow rate (Chapter III) of PPCPs and estrogens at STPs E and F from 2011 through 2014, which was shown in Appendix B. For population treated by each STP, 70,959 persons were put for STP-E and 109,300 for STP-F

while putting 98,576 for heads of livestock used for calculating VPs (Chapter IV). Based on the removal efficiency above (Table 7.2), PPCPs and estrogens introduced in the river from effluents of STP were predicted by using Equation 1.

Table 7.2 Volume of PPCPs and estrogens in possible generation per head of treating population based on the influent of STPs (M_{STP})

	M_{STP} (μg/day.person)							
	E STP				F STP			
	Spring	Summer	Fall	Winter	Spring	Summer	Fall	Winter
Acetaminophen	7.3	4.4	3.0	26.1	9.5	4.3	10.0	19.0
Caffeine	16.2	27.2	19.0	9.8	11.6	40.9	34.7	10.2
Ibuprofen	0.9	22.4	0.7	9.8	4.6	8.3	8.6	11.0
Naproxen	24.8	67.4	51.1	107.8	38.0	61.8	47.0	69.5
Theophylline	15.0	34.3	11.4	6.7	10.0	23.9	20.9	9.7
Ciprofloxacin	52.5	43.4	42.6	59.6	31.8	5.9	52.6	4.5
Sulpiride	301.3	149.4	228.1	345.1	229.9	145.8	146.6	287.1
Levofloxacin	135.3	94.5	111.1	149.1	92.6	15.9	13.8	10.7
DEET	118.0	187.5	15.5	12.4	68.0	130.7	30.2	9.9
Clarithromycin	111.7	59.0	173.6	183.4	106.5	74.9	137.2	213.3
Bezafibrate	4.0	10.1	21.3	57.2	18.3	18.5	60.3	82.4
Atenolol	119.0	106.6	121.2	115.2	25.6	16.9	35.6	30.9
Mefenamic_acid	49.3	77.5	54.1	47.2	89.1	92.6	96.8	79.4
Sulfamethoxazole	86.8	53.0	138.7	49.0	54.3	66.2	169.7	41.7
Ketoprofen	3.7	13.9	4.6	8.1	23.1	22.9	39.3	27.7
Roxithromycin	96.8	77.9	132.2	124.5	85.0	56.7	107.6	105.3
Furosemide	15.0	24.0	24.4	41.7	62.6	55.5	79.5	59.9
Sulfapyridine	12.8	67.2	67.6	35.3	54.7	48.3	77.7	32.5
Triclosan	6.0	-	5.0	-	22.4	29.0	13.1	26.4
Trimethoprim	49.4	13.0	27.5	29.8	35.8	26.8	24.2	36.2
Crotamiton	36.6	56.1	31.6	14.8	41.7	66.0	25.8	9.7
Carbamazepine	44.5	36.0	44.7	31.8	72.1	57.9	51.4	47.8
Triclocarban	13.4	19.0	17.0	14.8	13.2	39.5	13.5	23.3
Azithromycin	20.9	15.4	35.9	22.4	28.6	17.5	25.4	35.4
Oxytetracycline	0.3	19.1	23.1	0.6	-	0.4	1.1	0.2
Lincomycin	23.8	23.5	24.3	40.4	79.8	41.4	90.0	71.6
Diclofenac	31.5	19.9	33.9	31.1	57.5	47.2	53.5	30.5
Sulfadimidine	1.2	1.3	0.9	0.2	27.4	38.7	167.0	7.8
Estriol	-	21.2	57.5	13.5	-	23.0	55.4	16.9
Enrofloxacin	4.3	-	0.4	3.0	19.1	-	4.8	24.8
Norfloxacin	6.1	1.7	20.7	6.1	1.5	-	2.0	-
Diltiazem	16.4	14.4	17.5	13.8	16.6	16.6	14.9	13.8
Tetracycline	3.0	0.6	0.4	1.3	0.1	39.9	7.7	0.5
Erythromycin	8.1	-	8.3	17.6	19.2	-	9.2	3.0
Erythromycin-H2O	11.6	3.6	16.0	11.8	11.9	6.1	13.6	16.7
Propranolol	12.8	8.8	9.8	6.8	11.5	12.7	11.0	7.0
Fenoprofen	9.5	-	-	0.3	8.1	-	-	0.5
Estrone	0.1	0.3	5.9	0.2	0.9	2.1	6.4	1.2
Antipyrine	4.6	5.2	3.8	3.5	10.7	14.6	12.6	8.1
Indometacin	1.7	0.3	3.3	2.6	2.0	1.1	2.5	2.0
Estradiol	-	1.9	8.6	0.9	2.8	-	7.3	-
Primidone	1.9	1.6	1.8	2.8	2.0	6.0	14.3	3.6
Salbutamol	-	-	2.1	0.9	-	-	0.4	-
Metoprolol	0.8	0.8	1.8	0.9	2.4	1.4	2.1	1.3
Griseofulvin	1.5	-	-	0.8	2.0	-	-	0.3
Ethenzamide	0.1	0.3	0.6	1.6	0.3	0.6	0.6	0.9
Tylosin	0.5	0.7	2.0	1.0	1.2	1.7	2.7	2.7
2QCA	2.3	-	3.4	2.7	3.2	-	2.8	3.7
Isopropylantipyrine	1.6	0.9	1.2	2.5	7.1	2.1	1.7	2.4
Pirenzepine	-	-	-	-	0.2	-	0.5	-
Disopyramide	0.1	-	0.0	0.5	-	-	0.4	0.9
Dipyridamole	-	-	-	-	0.6	-	3.6	1.7
Clofibric_acid	-	-	-	-	-	-	3.2	0.7
Sulfathiazole	-	-	0.8	-	16.9	32.2	29.1	160.7
Sulfamerazine	-	-	-	-	-	-	0.2	-
Nalidixic_acid	-	-	-	0.1	-	-	-	0.7
Sulfamonomethoxine	-	-	-	-	-	-	-	-
Ceftiofur	-	-	-	-	0.3	-	-	3.1
Clenbuterol	-	-	-	-	-	-	-	-
Ifenprodil	-	-	-	0.2	-	-	-	-
Ethynylestradiol	-	-	-	-	-	-	-	-

※ - : Not detected or Not available

As a result of predicting based on the concentrations in influent of STPs, for STP-F, acetaminophen, sulpiride, clarithromycin, bezafibrate and sulfathiazole showed a high concentrations in effluent in the winter, while caffeine, DEET, crotamiton and triclocarban were predicted of high concentration in effluent in the summer. For STP-E, acetaminophen, naproxen, bezafibrate and erythromycin were predicted of high concentration in effluent in the winter, while caffeine, theophylline, mefenamic acid and crotamiton were predicted of high concentration in effluent in the summer. PPCPs and estrogens remaining in the effluents of STP cause problem by flowing in the river.

7.3.1.2 Modeling of predicted environmental concentrations

Concentration of PPCPs and estrogens in the river was predicted using the rate constant on photolysis, biodegradation and adsorption at experiments in Chapter VI and equation 2. With point s1 set for the upstream in the area of study, concentration of PPCPs and estrogens at point s7 finally inflow to Paldang Lake was predicted. For flow rate, we used the data at flow rate stream gauging station located at Gyeongan River using measurements for additional spots. Fig ure 7.3 shows the flow rates of each spot from 2011 through March 2014, used for calculating expression 2

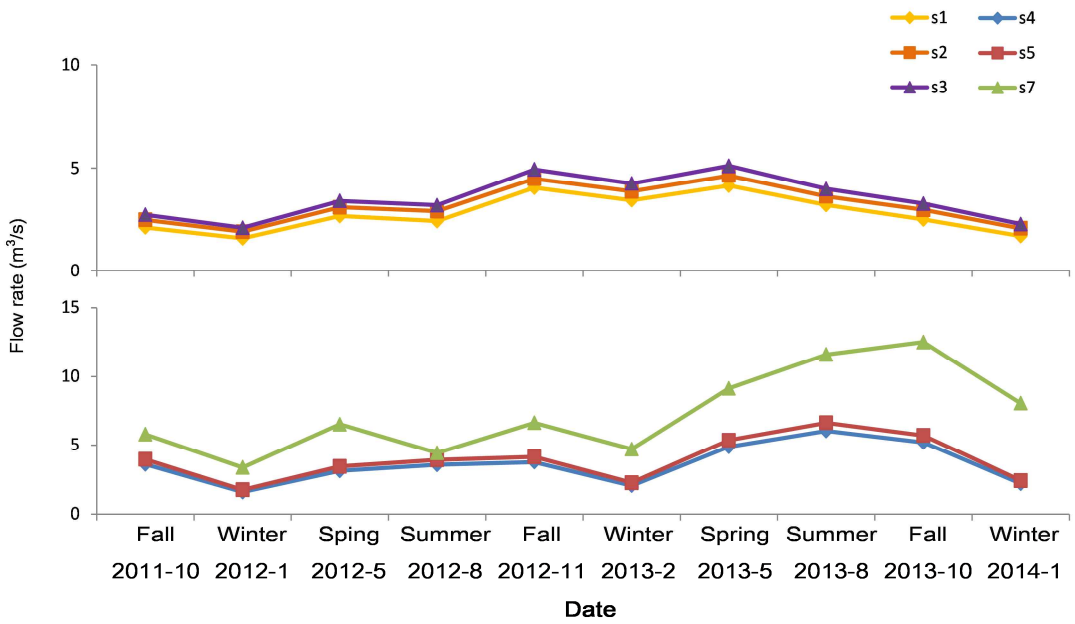

Figure 7.3 Flow rate (m^3/s) of Gyeongan River

Besides, for M_i, the seasonal mean values of PPCPs and estrogens remaining in effluent of STPs E and F were used for application (Table 7.3).

Table 7.3 Mass loading of PPCPs and estrogens from the STPs (M_i)

	M_i (g/day)							
	STP E				STP F			
	Spring	Summer	Fall	Winter	Spring	Summer	Fall	Winter
2QCA	0.17	0.16	0.27	0.23	0.58	0.34	0.61	0.55
Acetaminophen	0.44	0.34	0.20	2.04	0.98	0.51	0.87	2.12
Antipyrine	0.36	0.37	0.28	0.25	1.10	1.44	1.15	0.79
Atenolol	8.35	7.99	8.46	8.37	2.76	1.51	3.78	3.56
Azithromycin	2.05	0.57	1.96	1.69	3.99	2.93	3.25	3.79
Bezafibrate	0.30	1.09	1.15	2.88	1.99	1.77	5.28	8.75
Caffeine	1.12	1.89	1.38	0.71	1.25	4.07	3.49	1.07
Carbamazepine	4.03	2.86	3.01	2.61	7.67	5.61	5.22	4.87
Ceftiofur	-	-	-	-	-	-	-	-
Chlortetracycline	0.01	-	-	-	0.01	-	1.03	0.01
Ciprofloxacin	3.17	2.84	3.07	5.25	3.51	0.55	5.75	0.45
Clarithromycin	7.62	4.05	12.39	12.18	11.21	7.52	14.64	23.60
Clenbuterol	-	-	-	-	-	-	-	-
Clofibric_acid	-	-	0.01	-	0.12	0.02	0.24	0.08
Crotamiton	2.47	4.41	2.22	1.52	4.37	7.47	2.76	1.70
DEET	6.78	5.16	1.03	0.64	12.66	21.63	2.84	1.15
Diclofenac	3.75	1.03	3.15	3.30	6.18	5.02	5.84	5.03
Diltiazem	1.15	1.03	1.22	1.02	1.76	1.60	1.62	1.54
Dipyridamole	-	-	-	-	-	-	0.33	0.01
Disopyramide	-	-	-	0.01	-	-	0.05	0.01
Enrofloxacin	0.53	-	0.04	0.08	0.67	-	6.01	0.08
Erythromycin	0.66	-	0.96	1.20	1.32	-	0.00	0.95
Erythromycin-H2O	0.80	0.34	1.10	0.79	1.27	0.59	1.46	0.97
Estradiol	-	0.01	-	-	-	-	-	-
Estriol	-	-	-	-	-	-	-	-
Estrone	0.02	0.01	0.02	0.01	0.10	0.16	0.42	0.09
Ethenzamide	0.09	0.04	0.13	0.11	0.17	0.02	0.10	0.14
Ethynylestradiol	-	-	-	-	-	-	-	-
Fenoprofen	-	-	-	0.02	-	-	-	-
Furosemide	0.96	1.90	1.46	3.06	6.79	5.32	8.17	6.96
Griseofulvin	0.09	-	-	0.02	0.22	-	-	-
Ibuprofen	0.07	2.06	0.06	0.70	0.51	0.54	0.88	1.27
Ifenprodil	-	-	-	-	-	-	0.09	-
Indometacin	0.12	0.02	0.19	0.20	0.21	0.10	0.32	0.26
Isopropylantipyrine	0.28	0.14	0.21	0.18	0.58	0.34	0.23	0.28
Ketoprofen	0.18	1.18	0.21	0.66	2.48	2.25	4.38	3.40
Levofloxacin	9.69	6.90	8.22	12.44	6.74	1.39	1.76	1.03
Lincomycin	1.49	1.72	2.20	2.84	4.14	4.05	6.62	7.38
Mefenamic_acid	3.75	6.22	3.95	3.18	9.44	8.98	10.26	7.31
Metoprolol	0.06	0.06	0.10	0.08	0.19	0.11	0.21	0.15
Nalidixic_acid	-	-	-	-	-	0.08	0.09	0.02
Naproxen	1.79	5.74	3.78	8.64	3.90	6.10	5.06	7.74
Norfloxacin	0.25	0.14	0.15	0.26	0.16	-	3.67	-
Oxytetracycline	0.05	-	0.11	0.04	-	0.03	0.29	0.03
Pirenzepine	-	-	-	-	-	-	-	-
Primidone	0.29	0.18	0.32	0.22	0.49	0.39	0.32	0.57
Propranolol	1.13	1.04	1.00	0.85	1.24	1.20	1.47	1.18
Roxithromycin	6.69	5.00	9.02	8.79	8.98	5.57	10.47	10.89
Salbutamol	-	-	-	0.04	-	-	-	-
Sulfadimethoxine	0.01	-	-	-	0.08	0.15	0.11	0.10
Sulfadimidine	0.12	0.10	0.09	0.03	3.24	4.05	25.25	0.68
Sulfamerazine	-	-	-	-	-	-	0.05	0.03
Sulfamethoxazole	6.20	6.52	7.83	3.64	5.79	6.43	19.97	4.18
Sulfamonomethoxine	-	-	-	-	0.01	-	0.12	-
Sulfapyridine	2.00	4.40	4.54	2.58	2.51	4.50	5.94	3.41
Sulfathiazole	-	-	0.01	-	1.78	3.27	3.59	8.52
Sulpiride	18.66	10.89	15.85	24.44	22.85	14.28	15.82	31.29
Tetracycline	0.03	0.05	0.03	0.08	0.01	0.02	0.55	0.06
Theophylline	1.04	2.77	0.81	0.52	1.09	2.36	2.35	1.15
Thiamphenicol	-	-	-	-	-	-	-	-
Tiamulin	-	-	0.03	0.01	0.68	0.47	2.36	1.85
Triclocarban	0.84	0.56	0.95	0.21	1.11	1.64	0.85	0.08
Triclosan	0.45	-	0.33	0.00	1.73	1.81	1.74	0.23
Trimethoprim	3.03	0.92	1.69	3.08	3.77	2.63	2.70	3.60
Tylosin	0.05	0.03	0.10	0.08	0.17	0.03	0.23	0.25

※ – : Not detected or Not available

M_o used seasonal mean values of PPCPs and estrogens detected at each point shown in 5.3.3 of Chapter V (Appendix C). Besides, t_R and t_i were calculated using the mean flow velocity of Gyeongan River measured in the report. Mean flow velocity of Gyeongan River is 0.257 m/s with t_R and t_i of each point shown in Table 7.4.

Table 7.4 Travel time (t_R) and travel time from the STP (t_i)

t_R (day)	s1 > s2	0.25
	s2 > s3	0.19
	s3 > s4	0.21
	s4 > s5	0.09
	s5 > s7	0.16
	s6 > s7	0.11
t_i (day)	STP F > s2	0.22
	STP F > s3	0.40
	STP F > s4	0.62
	STP F > s5	0.71
	STP F > s7	0.86
	STP E > s7	0.01

Point s1 is the uppermost point in the study area and s2 the point of introducing effluent of STP-F, which meets small tributaries and flows into s7. Besides, s6 is the tributary located at Gyeongan River and flows into s7, which mixes s5, s6 and effluent of STP-E to be introduced to Paldang Lake. Loadings of PPCPs and estrogens were estimated by applying the factors calculated above to Equation 2. After applying reducing factors following the season and sampling point calculated in Chapter VI, PPCPs and estrogens estimated at each point of the river by season were put on Table 7.5.

Table 7.5 Estimated loading of PPCPs and estrogens at Gyeongan River

	C_{pec} Loading (g/day)																			
	Spring					Summer					Fall					Winter				
	s2	s3	s4	s5	s7	s2	s3	s4	s5	s7	s2	s3	s4	s5	s7	s2	s3	s4	s5	s7
2QCA	2.3	2.5	3.9	4.3	4.9	0.3	0.3	0.3	0.3	0.5	1.9	2.4	2.4	2.4	2.8	1.1	1.9	2.3	1.6	3.1
Acetaminophen	14.7	25.8	17.3	10.1	60.7	41.4	48.0	38.9	28.5	54.9	50.8	18.2	37.0	54.2	69.0	111.6	70.8	112.0	67.4	142.1
Antipyrine	1.1	3.9	3.4	4.7	4.7	1.4	3.3	3.4	5.2	4.1	1.1	1.4	2.7	3.2	3.7	0.9	1.9	2.1	1.5	2.5
Atenolol	3.1	9.8	7.3	5.2	16.0	1.5	4.4	4.4	5.8	13.3	5.1	14.3	11.9	8.4	21.7	5.3	11.3	11.5	7.6	24.0
Azithromycin	3.8	4.4	3.5	3.1	5.5	3.0	3.6	2.6	2.8	3.1	3.4	4.7	3.6	3.3	7.0	3.8	6.3	4.6	4.1	9.0
Bezafibrate	3.7	7.7	5.8	4.1	5.0	2.4	4.7	4.0	3.4	4.6	7.6	9.0	11.5	11.5	13.0	11.8	20.8	20.3	15.5	21.7
Caffeine	53.4	37.6	36.9	31.9	65.5	39.1	36.2	35.7	38.4	61.8	68.7	28.9	39.3	51.8	83.6	67.9	43.1	42.2	27.5	63.6
Carbamazepine	11.6	23.9	25.1	21.6	34.8	7.9	16.3	15.2	17.5	23.8	9.6	17.5	18.6	20.9	34.6	7.6	14.9	14.9	11.4	25.6
Ceftiofur	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ciprofloxacin	0.2	0.2	0.1	0.3	3.0	0.2	0.3	0.2	1.0	3.4	2.2	1.3	1.5	1.0	4.8	0.4	0.8	0.7	0.6	6.2
Clarithromycin	14.7	31.1	28.7	22.8	36.8	9.0	18.4	15.8	17.9	21.9	19.0	39.2	42.2	41.9	72.5	28.2	59.2	53.4	40.5	89.6
Clenbuterol	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1
Clofibric_acid	0.2	0.3	0.3	0.3	0.3	0.0	0.1	0.1	0.0	0.0	0.6	0.7	0.4	0.4	0.9	0.1	0.3	0.2	0.2	0.3
Crotamiton	6.2	14.2	14.6	13.3	24.4	29.2	27.1	28.6	49.8	52.2	7.3	11.8	13.3	15.0	30.1	3.5	6.3	6.1	4.2	12.5
DEET	19.9	38.5	40.4	36.0	56.7	30.5	71.7	60.1	71.9	80.7	7.4	10.5	12.5	14.9	25.6	2.1	4.5	4.5	3.3	6.6
Diclofenac	1.3	1.2	0.4	0.6	4.1	2.1	2.0	0.8	0.3	1.6	4.8	6.9	5.4	5.2	11.5	4.3	7.0	5.4	3.5	10.0
Diltiazem	1.9	3.6	2.7	2.3	3.8	1.7	3.3	2.4	2.4	3.6	2.4	3.5	3.9	3.8	6.3	1.9	3.6	3.5	2.6	5.6
Dipyridamole	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.1	0.1	0.1	0.0	0.1	0.0	0.0	0.0	0.1
Disopyramide	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4	0.1	0.1	0.4	0.7	0.1	0.1	0.1	0.1	0.3
Enrofloxacin	0.0	0.0	0.0	0.5	0.5	0.0	0.0	0.0	0.0	0.0	0.6	0.1	0.2	0.3	0.4	0.0	0.0	0.5	0.1	0.2
Erythromycin	1.3	4.3	1.2	1.2	6.0	1.0	0.8	0.5	0.6	0.0	3.4	4.6	13.5	7.7	10.6	1.8	4.6	1.5	3.6	7.2
Erythromycin-H2O	2.1	4.2	4.3	3.5	5.9	1.4	2.5	2.0	3.0	3.7	4.5	5.0	14.6	9.0	11.6	1.5	3.1	3.0	2.3	5.8
Estradiol	0.0	0.0	0.0	0.0	0.0	0.1	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Estriol	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Estrone	0.4	0.6	0.5	0.4	0.8	0.3	0.4	0.3	0.4	0.6	0.6	0.6	0.6	0.7	0.7	0.4	0.4	0.4	0.3	0.5
Ethenzamide	0.2	0.5	0.4	0.3	0.4	0.1	0.2	0.2	0.3	0.2	0.3	0.5	0.6	0.5	1.0	0.2	0.4	0.4	0.3	0.9
Ethynylestradiol	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Fenoprofen	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.3	0.3	0.2	0.0	0.2
Furosemide	1.0	0.5	0.1	0.0	0.9	1.3	0.4	0.1	0.3	1.8	4.3	4.6	1.8	1.9	2.2	4.4	4.5	2.6	1.4	4.6
Griseofulvin	0.2	0.2	0.2	0.2	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ibuprofen	4.1	12.5	6.6	4.9	12.1	3.1	6.1	4.7	4.9	10.3	9.6	5.9	8.9	8.7	15.7	16.2	13.2	16.5	10.3	18.7
Ifenprodil	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.1	0.2	0.0	0.0	0.0	0.0	0.0
Indometacin	0.2	0.5	0.2	0.2	0.7	0.1	0.1	0.1	0.1	0.1	0.4	1.4	1.2	0.6	1.6	0.5	0.6	0.5	0.3	0.7
Isopropylantipyrine	0.8	4.2	2.2	1.9	2.4	0.6	1.5	1.9	2.8	3.1	0.3	0.8	1.3	1.8	2.2	0.5	1.1	1.3	1.0	1.8
Ketoprofen	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.9	0.5	0.1	0.0	0.0	0.2	0.6	0.2	0.1	0.0	0.7
Levofloxacin	8.0	10.2	8.4	7.0	19.6	3.7	4.4	3.0	3.4	12.6	3.0	5.7	4.0	3.5	14.7	3.0	4.3	3.2	2.4	18.8
Lincomycin	4.6	12.3	12.5	9.5	13.6	4.3	10.0	8.4	9.7	12.2	7.2	11.9	15.7	17.2	20.4	8.3	19.6	15.5	12.6	27.3
Mefenamic_acid	12.0	24.1	20.8	19.3	30.3	10.3	21.3	17.4	19.0	29.3	12.9	20.1	24.6	26.4	35.4	9.7	21.6	19.2	10.2	25.9
Metoprolol	0.2	0.3	0.3	0.3	0.6	0.1	0.2	0.1	0.1	0.2	0.5	0.6	0.6	0.6	1.0	0.2	0.4	0.5	0.4	0.7
Nalidixic_acid	0.0	0.0	0.0	0.0	0.0	0.4	0.3	0.0	0.4	0.0	0.1	0.1	0.6	0.6	0.7	0.1	0.2	0.1	0.2	0.1
Naproxen	5.1	10.1	7.4	6.5	13.9	6.5	14.8	9.3	9.2	19.9	11.5	16.2	15.2	16.8	23.6	13.3	22.8	20.3	15.1	34.2
Norfloxacin	0.0	0.1	0.1	0.2	0.5	0.0	0.0	0.0	0.0	0.1	1.2	0.5	0.7	0.4	0.9	0.0	0.1	0.0	0.1	0.3
Oxytetracycline	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.4	7.1	0.5	0.1	2.0	0.0	0.1	0.1	0.0	0.1
Pirenzepine	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.5	0.0	0.0	0.0	0.0	0.0
Primidone	0.5	1.4	1.4	1.3	1.3	0.4	1.0	0.9	1.4	1.8	0.6	0.4	1.1	1.1	2.1	0.7	1.3	1.1	1.1	1.3
Propranolol	0.9	1.4	0.9	0.7	1.9	0.9	1.8	1.2	1.1	2.2	1.6	3.1	2.9	2.7	4.9	1.3	3.1	2.6	1.9	4.6
Roxithromycin	11.0	23.2	21.6	17.3	27.3	6.1	12.7	10.5	11.5	16.0	13.0	24.8	27.8	27.5	44.0	12.9	27.1	25.5	19.3	42.9
Salbutamol	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sulfadimidine	3.3	8.7	7.7	7.0	7.1	3.8	11.1	6.6	7.3	6.9	24.6	26.8	40.1	35.0	33.6	0.7	2.4	2.5	1.7	1.9
Sulfamerazine	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.1	0.0	0.0	0.0	0.1	0.1	0.0	0.1
Sulfamethoxazole	9.0	20.6	20.3	20.2	29.2	6.8	18.7	15.2	20.0	30.3	22.1	27.9	40.6	41.0	54.9	7.0	16.8	17.6	12.7	22.6
Sulfamonomethoxine	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.6	0.2	0.7	0.0	0.0	0.0	0.0	0.1
Sulfapyridine	2.9	6.2	5.3	4.2	7.5	4.5	8.7	6.4	6.9	12.0	12.3	15.6	14.6	15.9	24.3	6.2	7.4	6.2	5.6	12.0
Sulfathiazole	2.1	4.3	3.9	3.3	3.8	3.2	9.4	5.3	6.3	5.7	4.1	5.2	7.5	6.7	7.9	8.5	10.8	10.1	8.9	9.2
Sulpiride	26.5	79.5	86.1	70.8	122.3	17.6	48.3	45.5	53.4	67.1	21.6	50.7	57.4	66.0	113.7	41.9	91.0	91.0	65.3	138.8
Tetracycline	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.4	0.8	0.8	0.2	0.4	0.0	0.1	0.0	0.0	0.1
Theophylline	8.3	11.6	10.9	9.3	19.1	6.3	13.3	12.2	15.5	22.2	10.3	10.2	12.9	16.0	23.7	10.1	11.0	11.4	8.6	18.5
Triclocarban	2.3	2.3	3.0	2.4	5.0	3.3	3.9	2.7	2.8	2.1	3.8	2.9	6.3	3.0	5.8	1.5	1.1	1.5	0.8	2.0
Triclosan	1.7	1.7	1.7	1.7	2.2	4.0	3.3	2.9	4.8	1.8	1.7	1.7	2.9	2.6	2.1	0.2	1.9	1.7	0.5	0.5
Trimethoprim	3.9	8.7	8.6	6.9	12.1	2.7	6.2	4.9	5.2	6.1	3.4	4.2	6.2	5.7	9.2	4.1	8.4	8.2	6.2	14.9
Tylosin	0.4	0.3	0.3	0.2	0.2	0.1	0.1	0.1	0.0	0.1	0.7	0.3	0.8	0.7	1.1	0.5	0.7	0.6	0.4	0.9

With introduction of tributary of s6 and effluent of STP-E, s7 was estimated to have a high C_{PEC}. At s7, a point right before the introduction into Paldang Lake, acetaminophen and naproxen, which are used for analgesic, as well as clarithromycin, lincomycin and roxithromycin, which are antibiotics, were estimated to have a higher C_{PEC} in summer than in winter. Substance with a high estimate of C_{PEC} in summer included crotamiton, which is used for itchiness, insecticide DEET and sulfadimidine, which is often used for antibiotic on livestock. For caffeine, sulpiride, DEET, clarithromycin and acetaminophen, which are substances with a high estimated concentration, the estimated concentration and surveyed concentration by season were put in Figure 7.4.

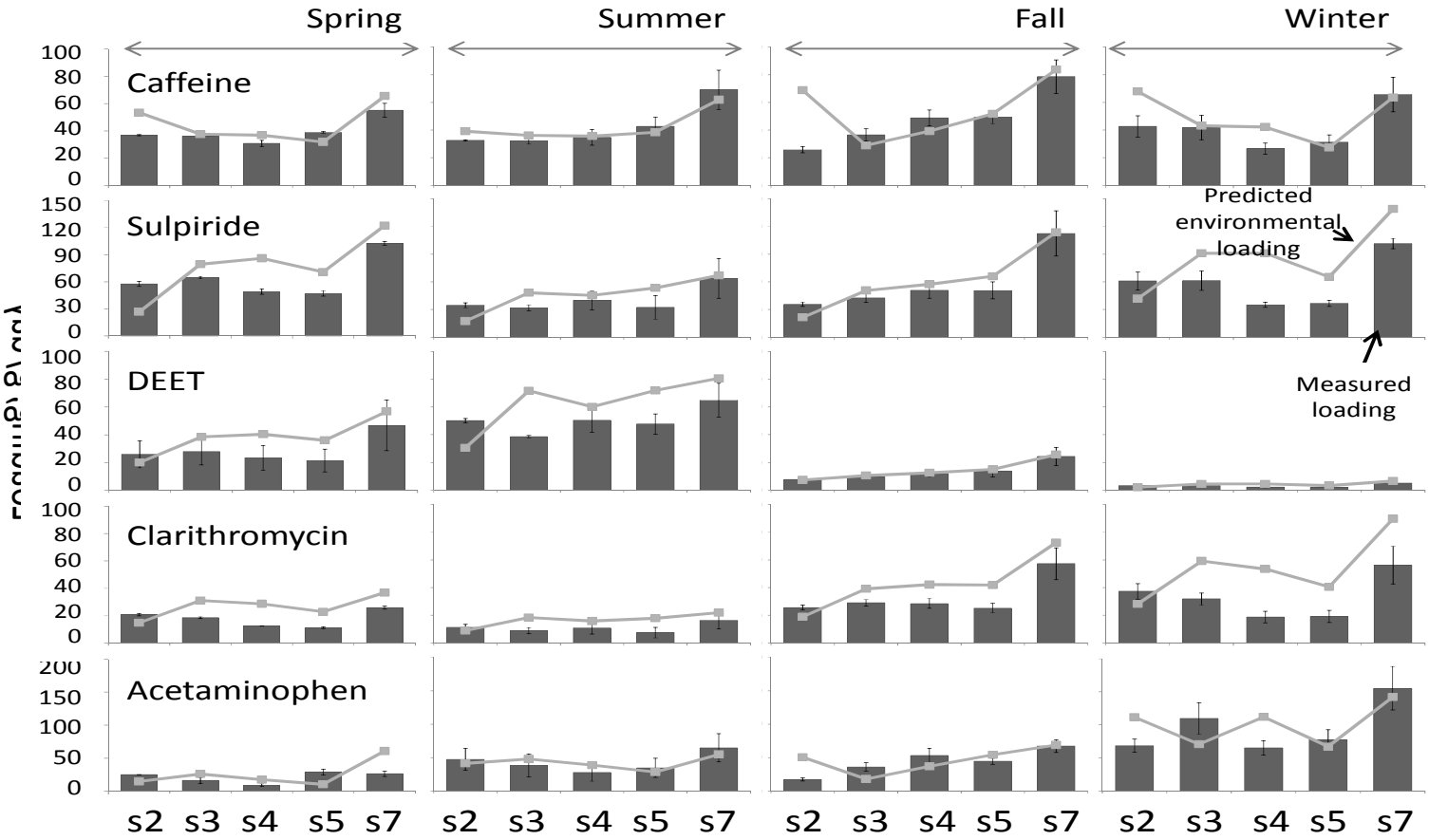

Figure 7.4 C_{PEC} of caffeine, sulpiride, DEET, clarithromycin and acetaminophen predicted in the river by season considering time of flow, photolysis, biodegradation and adsorption

C_{PEC}, an estimated loading using Equation 2, were compared with survey measures at Gyeongan River from 2011 through 2014. Estimated loading showed a tendency similar to actual results of measure. However, there arose the problem of a low accuracy of estimated concentration of s2 point because of the pollution source located in the upper stream of s2 point. Still, this study had limitations that could not consider all STPs and pollution sources located out of our study area.

7.3.1.3 Modeling of predicted environmental concentrations of veterinary pharmaceuticals

Table 7.6 shows predicted concentration of chlortetracycline, tiamulin, sulfadimethoxine, thiamphenicol, which are the substances detected only from livestock wastewater (Chapter IV), by season. However, as it was impossible to grasp the exact heads of livestock (MOE 2010), these are the predicted values assuming that they are all introduced in STP F which processes all livestock wastewater of Gyeongan River. There were 98,576 heads of cows, pigs and hens bred in the study area, but being unable to know the number of livestock by season, the investigated number of animals was used for estimation (MOE 2010).

Table 7.6 Predicted values of VPs based on the influent of STP-F

	STP F			
	M_{STP} (ng/day.head)			
	Spring	Summer	Fall	Winter
Chlortetracycline	1,182	-	9,846	12,027
Tiamulin	5,264	3,899	11,421	23,060
Sulfadimethoxine	1,242	3,802	1,820	2,001
Thiamphenicol	0.041	0.044	0.039	2,715

Though showing the high removal efficiency over 90 %, chlortetracycline decreased in removal efficiency to 87.06 % in the winter, which increased the predicted effluent. The rest matters showed low removal efficiencies and these are substances that increase the outflow into the river with increase of use. Then, for tiamulin, sulfadimethoxine, chlortetracycline and thiamphenicol which were detected only from livestock wastewater, M_{STP} was estimated using Equation 2 (Figure 7.4).

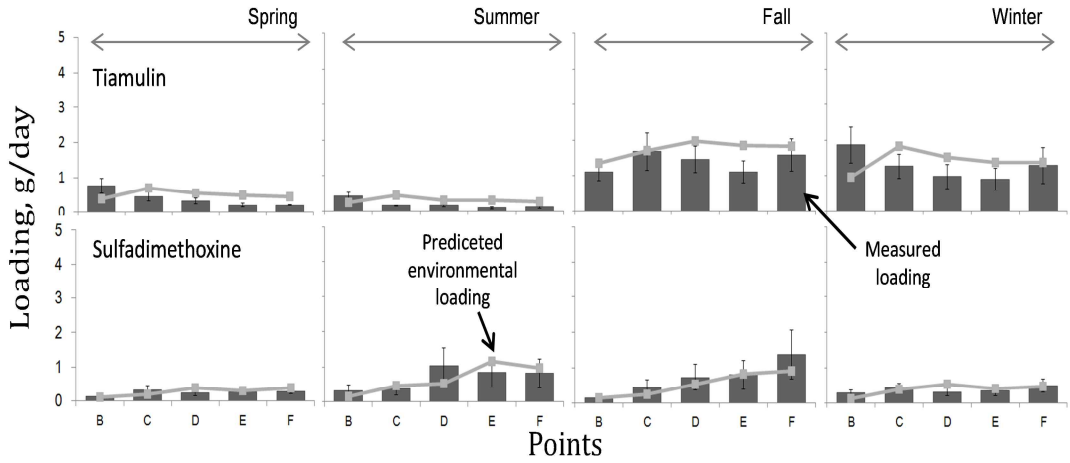

Figure 7.5 Estimated loading of tiamulin and sulfadimethoxine at the river using equation 2

In Korea, tiamulin, which is much used by adding to the pigs or chickens feed, and sulfadimethoxine, which is mainly used for animals' treatment by infection, showed a tendency of similar survey measure and predicted measure in the river. Detection of tiamulin used for pig's pneumonia or hen's inflammation increased in fall and winter, while sulfadimethoxine used against parasites was estimated with a higher detection in summer and fall. Since the model is a prediction based on influent, it is also considered suitable for VPs. However, chlortetracycline and thiamphenicol were excluded from estimation because they existed in the environment with concentrations lower than the limitation of detection.

7.3.2 Summary of scenarios

The Gyeongan River area is marked by rapid population growth and is thus at increased risk of exposure to PPCPs and estrogens. To establish an action plan to reduce the ecotoxicity of the Gyeongan River, we set up a number of conceivable scenarios for the PPCPs and estrogens that are discharged into it. Prior to setting up the scenarios, we precisely identified all pollution sources to enable efficient management of the PPCPs and estrogens that are discharged into the Gyeongan River.

7.3.2.1 Management of pollution sources influent from upriver and tributary

With pollution sources influent from other than the study area shown in Figure 7.6, the upper stream areas of s1 was marked off as A1-5 and of the tributary (s6) as B1. In these areas lie big or small treating plants, most of which are small-sized and treating sewage with MBR, SBR and NBS systems.

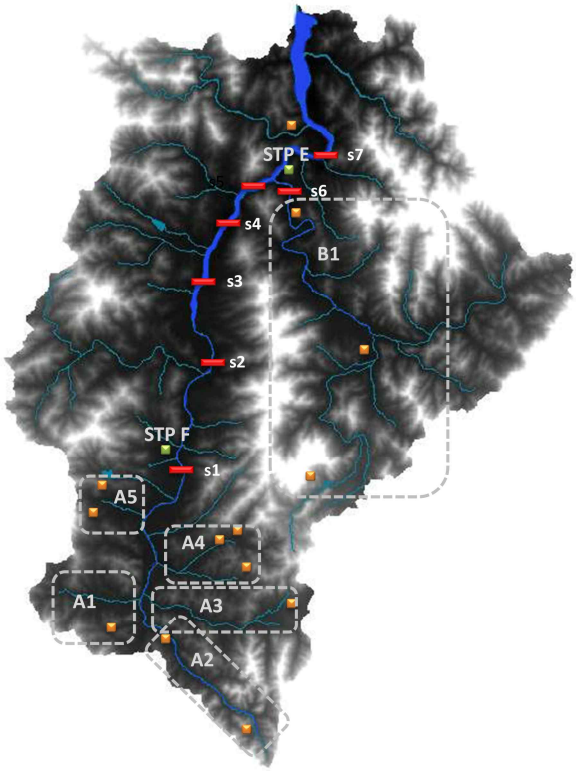

Figure 7.6 Major pollution sources influent to the upstream and tributary of Gyeongan River

The Figure 7.7 shows the present condition of PPCP and estrogen generations at Gyeongan River in division into the regions of A1-5, B1 and STP E and F.

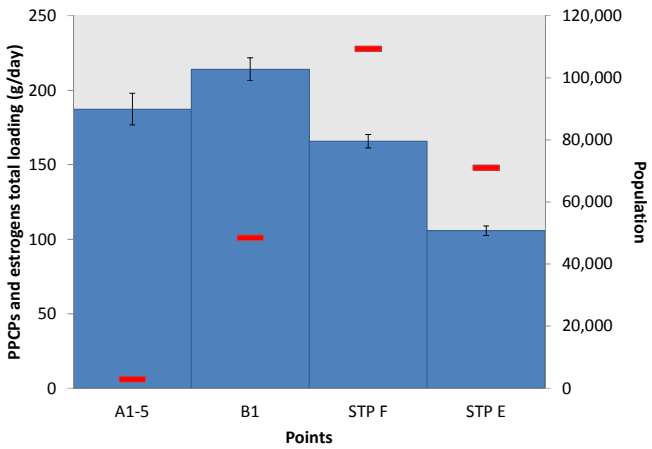

Figure 7.7 Total loadings of PPCPs and estrogens occurring at each spot and treating populations

Compared to treating populations, A1-5 and B1 regions showed high loadings of PPCPs and estrogens, based on which result the scenario was composed.

7.3.2.2 Scenario I and II

Scenario I and II was based on the removal rates of the various processing methods, as explained in Chapter III. The A2O system is the most efficient bioprocessing method for removing PPCPs and estrogens, and the UV disinfection system is highly efficacious. Consequently, scenario I applied the removal rates of the A2O and UV treatments as the MLE and UV treatments in STP E. Scenario II applied the removal rates of the A2O process and UV disinfection in A1-5, B1, and STPs E and F. For STP F, which uses a B3 process and chlorine treatment method, we retained the existing biological treatments and replaced the chlorine treatment with an UV disinfection system because of its thoroughness in treating livestock wastewater. However, given that the UV disinfection systems that are installed in conventional STPs are designed for disinfection purposes and not for the removal of PPCPs and estrogens, any considerable reductions could not be expected from adding conventional treatment methods to the wastewater treatment process.

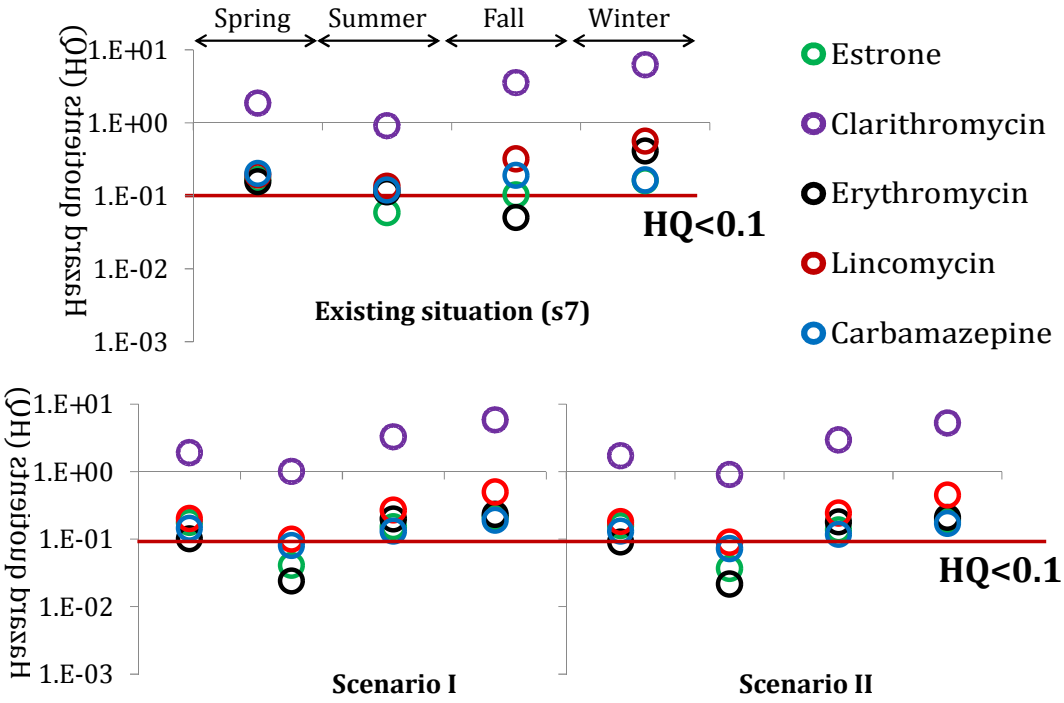

Figure 7.8 Results of hazard quotients by scenario I and II

In scenario I and II, difficulties were encountered in increasing the PPCPs and estrogen removal rates and lowering the HQs with the existing facilities of the STPs.

7.3.2.3 Scenario III, IV, V, and VI

Scenarios III, IV, V, and VI were based on the results of studies investigating the UV- and

ozone-based treatments of PPCPs and estrogens (Table 7.7 and 7.8).

In scenarios III and IV, the PPCPs and estrogen concentrations and HQs in the Gyeongan River were predicted and calculated assuming the use of UV and ozone treatments, respectively, after the biological treatments in STPs E and F. Besides the substances that are discharged from STPs E and F, the Gyeongan River is also affected by the effluents from small treatment facilities that are situated at study sites A1–5 upstream and B1 in an affluent branch. Scenarios V and VI considered the values resulting from the biological treatments and subsequent UV and ozone treatments, respectively, in all of the major and minor wastewater treatment facilities (STPs E and F, A1-5, and B1).

Table 7.7 Removal efficiency of the PPCPs and estrogens for UV process (UV : 0.639 mW/cm^2)

No.	Compounds	Removal efficiency (%)	Ref.
1	Acetaminophen	31	Ilho Kim 2008
2	Atenolol	11	Ilho Kim 2008
3	Azithromycin	54	Ilho Kim 2008
4	Bezafibrate	-	-
5	Caffeine	17	Ilho Kim 2008
6	Carbamazepine	93	Ilho Kim 2008
7	Ciprofloxacin	21	Ilho Kim 2008
8	Clarithromycin	-	-
9	Clenbuterol	98	Ilho Kim 2008
10	Clofibric_acid	50	Ilho Kim 2008
11	Crotamiton	20	Ilho Kim 2008
12	DEET	98	Ilho Kim 2008
13	Diclofenac	100	Ilho Kim 2008
14	Diltiazem	98	Ilho Kim 2008
15	Dipyridamole	94	Ilho Kim 2008
16	Disopyramide	2	Ilho Kim 2008
17	Erythromycin	2	Ilho Kim 2008
18	Erythromycin-H2O	-	-
19	Estradiol	-	-
20	Estriol	-	-
21	Estrone	21	Broseus et al., 2009
22	Ethenzamide	-	Ilho Kim 2008
23	Ethynylestradiol	86	Broseus et al., 2009
24	Furosemide	50	Ilho Kim 2008
25	Griseofulvin	74	Ilho Kim 2008
26	Ifenprodil	92	Ilho Kim 2008
27	Isopropylantipyrine	97	Ilho Kim 2008
28	Ketoprofen	30	Ilho Kim 2008
29	Levofloxacin	22	Ilho Kim 2008
30	Lincomycin	25	Ilho Kim 2008
31	Mefenamic_acid	22	Ilho Kim 2008
32	Metoprolol	87	Ilho Kim 2008
33	Nalidixic_acid	22	Ilho Kim 2008
34	Naproxen	21	Ilho Kim 2008
35	Pirenzepine	13	Ilho Kim 2008
36	Primidone	35	Ilho Kim 2008
37	Propranolol	10	Ilho Kim 2008
38	Roxithromycin	84	Ilho Kim 2008
39	Sulfadimethoxine	94	Ilho Kim 2008
40	Sulfamethoxazole	11	Ilho Kim 2008
41	Theophylline	-	-

Table 7.8 Removal efficiency of the 41 PPCPs and estrogens for O_3 process

(Contact time: 10 min)

No.	Compounds	O_3 dose 2mg/L	4mg/L	6mg/L	Ref.
1	Acetaminophen	> 95	-	-	Marc M. et al., 2005
2	Atenolol	89	> 98	> 98	Ilho Kim 2008
3	Azithromycin	97	100	100	Ilho Kim 2008
4	Bezafibrate	83	99	100	Ilho Kim 2008
5	Caffeine	80	80	0	Marc M. et al., 2005
6	Carbamazepine	100	100	100	Ilho Kim 2008
7	Ciprofloxacin	93	> 97	> 95	Ilho Kim 2008
8	Clarithromycin	90	99	100	Ilho Kim 2008
9	Clenbuterol	38	-	-	Marc M. et al., 2005
10	Clofibric_acid	74	84	> 97	Ilho Kim 2008
11	Crotamiton	100	100	100	Ilho Kim 2008
12	DEET	67	88	93	Ilho Kim 2008
13	Diclofenac	> 98	> 97	> 98	Ilho Kim 2008
14	Diltiazem	100	100	100	Ilho Kim 2008
15	Dipyridamole	100	100	100	Ilho Kim 2008
16	Disopyramide	74	96	100	Ilho Kim 2008
17	Erythromycin	100	100	100	Ilho Kim 2008
18	Erythromycin-H2O	100	100	100	Ilho Kim 2008
19	Estradiol	> 90	-	-	R. Broseus et al., 2009, Marc M. et al., 2005
20	Estriol	> 90	-	-	R. Broseus et al., 2009, Marc M. et al., 2005
21	Estrone	> 90	-	-	R. Broseus et al., 2009, Marc M. et al., 2005
22	Ethenzamide	100	100	100	Ilho Kim 2008
23	Ethynylestradiol	> 90	90	-	R. Broseus et al., 2009, Marc M. et al., 2005
24	Furosemide	> 99	100	100	Ilho Kim 2008
25	Griseofulvin	62	86	98	Ilho Kim 2008
26	Ifenprodil	97	100	100	Ilho Kim 2008
27	Isopropylantipyrine	> 98	> 97	> 97	Ilho Kim 2008
28	Ketoprofen	73	91	97	Ilho Kim 2008
29	Levofloxacin	98	100	98	Ilho Kim 2008
30	Lincomycin	> 99	> 99	> 99	Ilho Kim 2008
31	Mefenamic_acid	> 98	> 98	> 98	Ilho Kim 2008
32	Metoprolol	86	> 99	> 99	Ilho Kim 2008
33	Nalidixic_acid	66	96	> 99	Ilho Kim 2008
34	Naproxen	86	83	89	Ilho Kim 2008
35	Pirenzepine	96	96	95	Ilho Kim 2008
36	Primidone	51	85	87	Ilho Kim 2008
37	Propranolol	98	98	98	Ilho Kim 2008
38	Roxithromycin	100	98	100	Ilho Kim 2008
39	Sulfadimethoxine	100	100	100	Ilho Kim 2008
40	Sulfamethoxazole	97	100	100	Ilho Kim 2008
41	Theophylline	96	99	99	Ilho Kim 2008

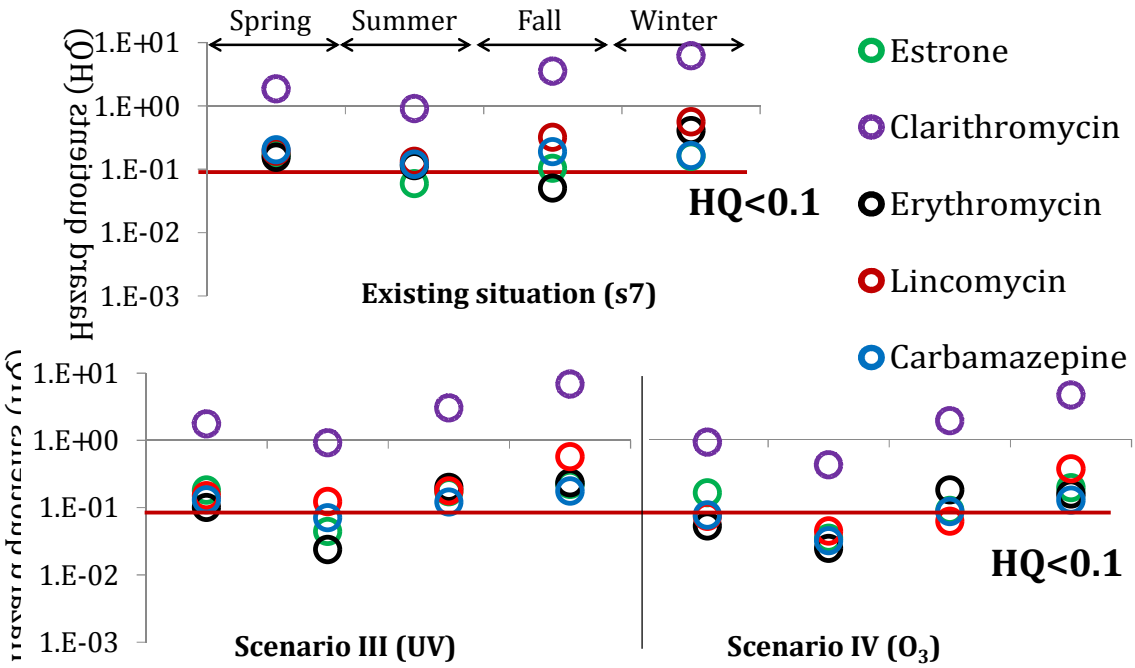

Figure 7.9 Results of hazard quotients by scenario III (UV treatment) and IV (O_3 treatment) in STPs E and F

UV treatment was found to be less efficacious than ozone treatment because its performance widely varied for different substances. Scenario III showed no effects in reducing clarithromycin with the highest average HQ in the Gyeongan River. Its concentration was reduced in scenario IV, but it still showed an average HQ exceeding 1. No considerable reductions in HQs were expected for the other substances. Besides the substances that are discharged from STPs E and F, the Gyeongan River is also affected by the effluents from small treatment facilities that are situated at study sites A1–5 upstream and B1 in an affluent branch. Scenarios V and VI considered the values resulting from the biological treatments and subsequent UV and ozone treatments, respectively, in all of the major and minor wastewater treatment facilities (STPs E and F, A1-5, and B1).

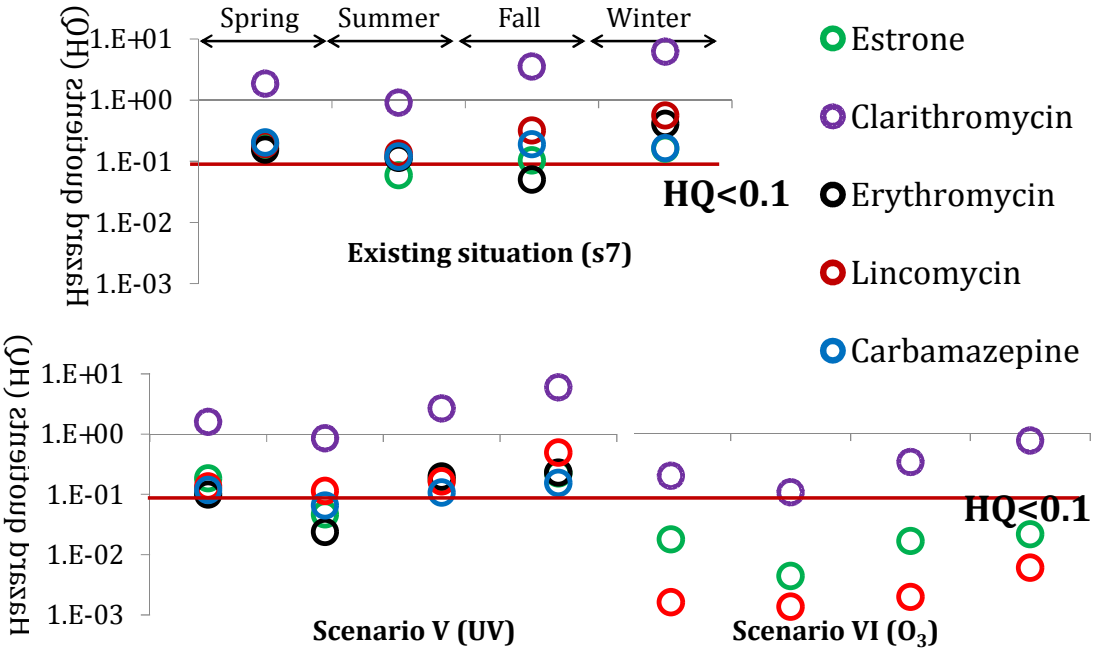

Figure 7.10 Results of hazard quotients by scenario V (UV treatment) and VI (O_3 treatment : 2 mg/L) in A1-5, B1, and STPs E and F

In Scenario V, in which UV treatment was applied, reductions were achieved for most substances, but clarithromycin and its toxic effects on the river still showed an average HQ exceeding 1, and those of carbamazepine, lincomycin, and estrone were 0.1 or higher. Scenario VI yielded considerable reductions in the HQs for most substances. In particular, this was the only scenario in which the HQ of clarithromycin was reduced to a ≤1 level in all seasons, with the other substances estimated at ≤0.1. However, clarithromycin, which exceeds 0.1 in fall and winter, is still causing the problem of ecological toxicity. Thus, in order to lower the HQ of clarithromycin below 0.1, we changed ozone treatment into 4 mg/L and calculated estimated HQ in the river.

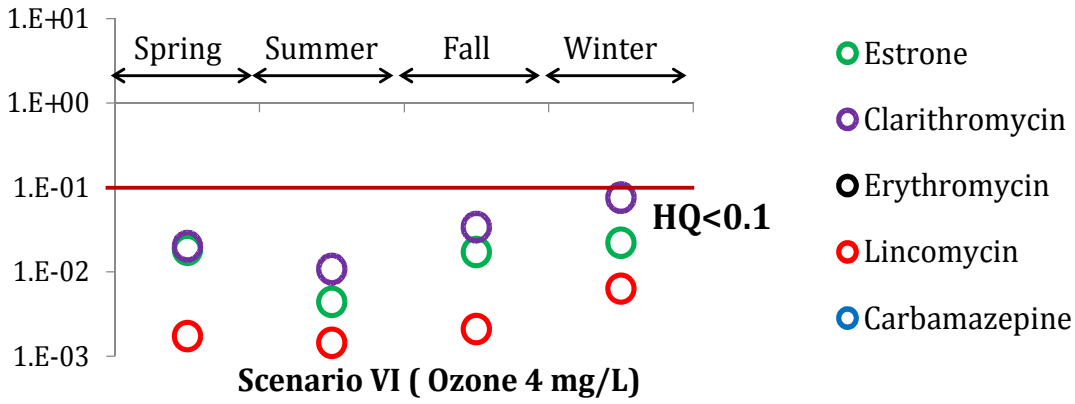

Figure 7.11 Results of hazard quotients by scenario VI (O_3 4 mg/L) in A1-5, B1, and STPs E and F

With an ozone treatment of 4 mg/L, it was possible to lower HQ below 0.1 at Gyeongan River (s7). Especially, with estimated HQ of 0.1 even in fall and winter, this method seems possible to reduce the influence on ecosystem.

7.3.3 Countermeasure

Based on the predicted values yielded by the above 6 scenarios, we concluded that only a limited degree of HQ reduction can be achieved through equipment upgrades of the biological treatment and disinfection systems of the wastewater treatment facilities in the Gyeongan River. Given that scenario VI, where ozone treatment was applied to the two STPs and minor facilities upstream and on an affluent branch of the Gyeongan River, yielded the best results in reducing HQs, the following variants of an action plan were established for minimizing the PPCPs and estrogensinduced contamination: installation of ozone treatment systems in the two STPs and minor facilities upstream and on an affluent branch of the Gyeongan River, or the construction of large STPs with ozone treatment equipment upstream and on the affluent branch to replace the existing small sewage treatment facilities. Either of these options will be conducive to protecting the aquatic ecosystems in the Gyeongan River and reducing the PPCPs and estrogens induced contamination of Paldang Lake, which is an important drinking water resource. With the current situation of the increasing amounts of the types, products, and consumption of PPCPs and the growing local populations near the Gyeongan River, the results of this study are expected to provide valuable data for the future management of PPCPs and estrogens.

7.3.4 Limitations of this model

This modeling uses a model of prediction based on the influent of PPCPs and estrogens in consideration of factors reduced in the river. Its merit is to manage the whole basin from PPCPs and estrogens with the minimum experiment. The existing modeling of relying on the use of

PPCPs and estrogens were hard to make either an exact distinction of substances or calculation on the excretions used in the human body. However, this model has some limitations. First it requires accurate information about the river basin and STPs. Since it is based on the influent of the STPs, it requires diverse information including processing population, influent, effluent, removal efficiency, UV value of reaching the river, flow rate and flow velocity. With more information of such, it is possible to predict more accurately. Another limitation is that it is not easy to consider nonpoint pollution sources. Beside this study had limitations that could not consider all STPs and pollution sources located out of our study area. Lastly, since this model was only on the target of Gyeongan River, it needs to be used for other rivers and to verify whether there is a reducing factor, besides photolysis, biodegradation and adsorption.

7.4 Conclusions

As a result of applying the model on the subject of Gyeongan River, PPCPs and estrogens between survey measure and estimated loading show a high degree of agreement.

1) Through generative predictions of STP-E and F by season, it was possible to know what the substances are likely to be imported into Gyeongan River. For STP-F, acetaminophen, sulpiride, clarithromycin, bezafibrate, sulfathiazole showed a high efflux in the winter, while caffeine, DEET, crotamiton, and triclocarban were predicted of high efflux in the summer. For STP-E, acetaminophen, naproxen, bezafibrate, erythromycin were predicted of high efflux in the winter, while caffeine, theophylline, mefenamic acid, crotamiton were predicted of high efflux in the summer.

2) As to substances of VPs, chlortetracycline showed a high predicted outflow in the winter while such substances with low removal efficiency as tiamulin, sulfadimethoxine and thiamphenicol were predicted to flow in the river in proportion to their volume of use. As a result of estimating the PPCPs and estrogens detected from the river based on PPCPs and estrogens introduced from STPs, survey measures and estimated loading by spot showed a high degree of agreement.

3) Using the estimated result, management method was proposed for substances with high estimated concentrations between PPCPs and estrogens introduced to Paldang Lake. The s7 point right before the influent to Paldang Lake, seeable increase in acetaminophen, caffeine, DEET, mefenamic acid, roxithromycin, crotamiton and sulpiride was estimated compared to s5. In addition to the reason for increase by the introduction from s5, effluent from STP-E is also the pollution source of s7. Though acetaminophen and caffeine show high removals efficiency of over 90 % at B3, MLE, CAS and A2O processes, they especially show as high a removal efficiency as over 99 % at A2O process. For Crotamiton, DEET, sulpiride and roxithromycin, there is no big difference in removal found in other processes.

4) Using six scenarios, we estimated PPCPs and estrogens in Gyeongan River. The existing treatment showed limitations in reducing PPCPs and estrogens. By adding ozone treatment to

small treatment facilities located at upper and lower reaches a river, as well as STP E and F, HQ was estimated below 0.1.

To reduce the contamination of Gyeongan River and Paldang Lake from PPCPs and estrogens, we could add ozone treatment process to STP by the method of scenario 2. The estimate of the concentration using the constructed model showed that it could decrease the existing contamination effectively. Besides, for effective control of PPCPs and estrogens, we can put Solids Retention Time (SRT) at over 7-10 days and increase the efficiency in removing bezafibrate, naproxen, estrone and levofloxacin (Chapter III).

7.5 References

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CHAPTER VIII

8 CONCLUSION AND RECOMMENDATIONS

8.1 Conclusions

Residual pharmaceuticals and personal care products (PPCPs) and estrogens have been recognized as emerging environmental pollutants and are widely distributed all over the world. These compounds cause bioaccumulation and biomagnification during present for a long time in the environment, thereby after adversely biota and human bodies. It is difficult to remove residual PPCPs and estrogens using conventional wastewater treatment because of resistant property to photodegradation, biodegradation, absorption and chemical decomposition. Moreover, data of Korea on the pollution of residual PPCPs and estrogens in rivers and lakes are limited. In this dissertation, species, sources, fate and risk of residual PPCPs and estrogens as well as behavior properties in river resources are demonstrated to encourage the domestic concern about residual PPCPs and estrogens. Moreover, this study was constructed the upgrade model to predict transport of frequently detected PPCPs, and endocrine disruptors in the river watershed of Korea. Main findings from this study are described below by each chapter.

In Chapter III, at six sewage treatment plants (STPs) in Korea, influent, secondary effluent and final effluent were examined from 2011 through 2014. Concentrations of PPCPs and estrogens detected from STPs in Korea and removal characteristics in diverse processes were verified. The main PPCPs found in Korean STPs during the research period were acetaminophen, caffeine, ibuprofen, naproxen, theophylline, ciprofloxacin, sulpiride, levofloxacin, DEET, clarithromycin, bezafibrate, atenolol, mefenamic acid, sulfamethoxazole, ketoprofen, and roxithromycin. Regarding the relative amounts of PPCPs, NSAIDs were most prevalent, followed by antibiotics, BLLAs, and estrogens. Diverse PPCPs and estrogens detected from STPs in Korea are being discharged into a river after their biological and chemical treatments. In the comparison of the removal efficiencies of the biological treatments of the STPs, the MLE and A2O processes were found to be more efficient than the CAS process in managing PPCPs effectively. In the case of treating livestock wastewater as well, the A2O process was found to be more efficient than the B3 process. Regarding the disinfection method, chlorination and sodium hypochlorite were found to be inefficient in removing PPCPs; thus, UV and ozone disinfections should be considered to reduce the amount of PPCPs flowing into rivers. There are a number of STPs in Korea using CAS process and chlorination. To protect a river from PPCPs and estrogens, it requires upgrade and addition of the process of the STPs. Effective method of managing above-mentioned substances at Gyeongan River can reduce PPCPs influent to Paldang Lake by shifting from MLE process of STP-E to A2O process. Still, this model had limitations that could not consider all STPs or pollution sources located out of our study area. This model was only on the target of Gyeongan River, it needs to be used for other rivers and to verify whether there is a reducing factor, besides photolysis,

biodegradation and adsorption.

In Chapter IV, methods of effective management were investigated by verifying Veterinary pharmaceuticals (VPs) detected from livestock wastewater occurring in the study area. Then, PPCPs and estrogens remaining in the sludge appearing in the process of wastewater treatment were verified to learn the risk of efflux. The STP is a facility that primarily treats livestock wastewater in HBR-II and then treats it with B3 process with wastewater. So analysis was made on PPCPs and estrogens included in livestock wastewater, excretions and sludge as well as influent and effluent of the STP. The VPs detected chiefly in the STP include tiamulin, chlortetracycline, sulfadimethoxine and thiamphenicol, while pharmaceuticals used by both animals and humans were found to be enrofloxacin, estrone, oxytetracycline, tylosin and sulfadimidine. Sulfadimethoxine and tiamulin with relatively low removal efficiency are considered to be VPs highly likely to flow out into the river. In controlling VPs at Gyeongan River, care must be taken of sulfadimethoxine and tiamulin highly likely to be discharged. It was verified that chlortetracycline and tiamulin detected from the river are mostly introduced from the effluent of STP. That is, chlortetracycline and tiamulin require management using the model and are the substances considered to minimize contamination of the river by treating them effectively at STP. Tiamulin as VPs can be more effectively treated in A2O and MLE processes than in B3 process of STP-F. Besides, as to sulfadimethoxine chemical treatment using ozone is more effective than chlorine disinfection, while chlortetracycline and tiamuline can be effectively treated using UV. Among PPCPs used by both animals and humans, for roxithromycin and sulpiride with a high concentration in effluent, we can increase removal efficiency with UV and ozone process. However, DEET, a substance with low removal efficiency, showed low removal efficiency at all STPs in the study area. As mentioned in Chapter III, however, using ozone or UV in the process of disinfection can also be a good way for effective management of PPCPs and estrogens.

In Chapter V, detection characteristics and present condition of PPCPs and estrogens detected from Gyeongan River located in the study area were verified. PPCPs and estrogens that show the highest composition in the influent of STPs in Korea are antibiotics and NSAIDs. Among the detected antibiotics, clarithromycin, lincomycin, erythromycin, levofloxacin and roxithromycin. Trimethoprim is a bacteriostatic antibiotic used mainly in the prophylaxis and treatment of urinary tract infections, and sulfamethoxazole is commonly used to treat urinary tract infections. Among the detected NSAIDs, acetaminophen, which is used as a fever reducer, ibuprofen and mefenamic acid, which are used as an anti-inflammatory PPCPs and a painkiller, and naproxen, which are antiphlogistics for arthritis, show high composition. Besides, the compounds detected in high concentration from all points are acetaminophen, caffeine, DEET, sulfamethoxazole and sulpiride. For PPCPs and estrogens by season, antipyrine, crotamiton, DEET, ethenzamide, primidone and sulfadimidine were detected in the high temperature in high concentration while in the low temperature acetaminophen, bezafibrate, chlortetracycline, fenoprofen, norfloxacin, sulpiride, tetracycline, thiamphenicol and tiamulin were characteristically detected in high concentration. Results of comparing compounds detected from the effluents of STP and the river showed that untreated PPCPs and estrogens are polluting the river. Concentrations of PPCPs and estrogens detected by season from Gyeongan River were used for projection model in Chapter VI and VII.

In Chapter VI, a model to effectively manage the PPCPs and estrogens introduced by diverse channels was investigated. There are a few modeling methods but each river has different conditions in microorganisms, sunlight and soil. Thus, this study is going to build a model suited for Gyeongan River in Korea. PPCPs and estrogens introduced into the river through diverse pathways flow to the lower stream with the river. While moving along the river, they are influenced by photolysis, biodegradation and adsorption. To install the factors of model, this study conducted experiments of photolysis, biodegradation and adsorption on the Gyeongan River. In photolytic experiment, a total of 28 substances, including 8 substances of NSAIDs, 15 of Antibiotics and the other 5, showed a decay rate over 10%. Biodegradation was conducted in division into upstream and downstream and the latter showed higher decay rates. PPCPs and estrogens with a decay rate over 10 % were sorted into 22 compounds. Other substances were under 10 % of decay rate, which was considered to have a low contribution to biodegradation. Lastly, since adsorption mostly showed a low decay rate, this study assumed that there is no change of PPCPs and estrogens studied caused by adsorption.

In Chapter VII, photolysis, biodegradation and adsorption of PPCPs and estrogens found in Chapter VI were implemented in the model to apply to Gyeongan River. Then, results of PPCPs and estrogens generated in the subject area verified in Chapter III, IV and V were used to build the model. As a result of applying the model on the subject of Gyeongan River, PPCPs and estrogens between survey measure and estimated loading show a high degree of agreement. Through generative predictions of STPs E and F by season, it was possible to know what the substances are likely to be imported into Gyeongan River. As a result of estimating the PPCPs and estrogens detected from the river based on PPCPs and estrogens introduced from STPs, survey measures and estimated loading by spot showed a high degree of agreement. Six scenarios to reduce the PPCPs and estrogens introduced to Gyeongan River were prepared and applied to Gyeongan River. By estimation, the existing treatment showed limitations to lower toxicity to ecosystem, especially with a problem in lowering HQ of clarithromycin in UV treatment. This necessitated ozone treatment to control clarithromycin, with the highest HQ in Gyeongan River, and other substances effectively. Besides STP E and F, we should also manage the pollution source influent from the treatment facilities located at the upstream and tributary in combination. Among many scenarios, it turned out that installation of ozone treatment at facilities of STP E and F, and A1-5 and B1 regions proved to lower HQ of the river most. Besides, an ozone concentration of 4 mg/L made HQ of PPCPs and estrogens below 0.1 successfully lowering toxicity given to ecosystem.

8.2 Recommendations for future research

1) This study was made on the subject of PPCPs and estrogens flowing into STP. However, we have failed to study whether the existing process of treatment can cover the influx of high-concentration PPCPs or estrogens into STP. Besides, treatment PPCPs in chemical process can generate by-products. To remove PPCPs effectively, it is needed to study on generation of by-products and ecological risk.

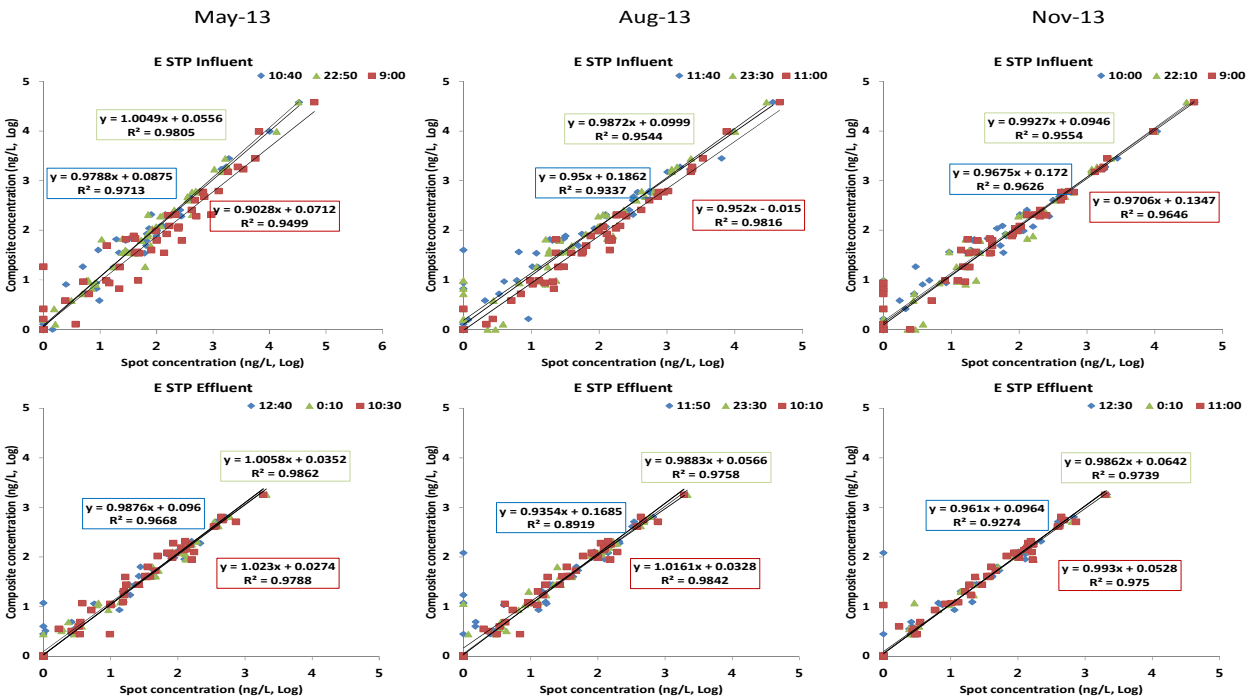
2) Estrogen, the matter of de-conjugation and conjugation, requires study on its change

and behavior at the process of STPs. Besides, regarding synthetic estrogens and other PPCPs, we need to examine their change, behavior and potential for toxicity in aquatic environment.

3) Though this model has been built to apply to Gyeongan River, we can also apply to other rivers by resetting factors. It is needed to apply this model to rivers and STP in other region or country to work on the management of PPCPs and estrogens and upgrade of the model.

BIBLIOGRAPHY

Appendix A. Comparison of PPCPs and estrogens by spot sampling and composite sampling in May, Aug and Nov for STP E and F



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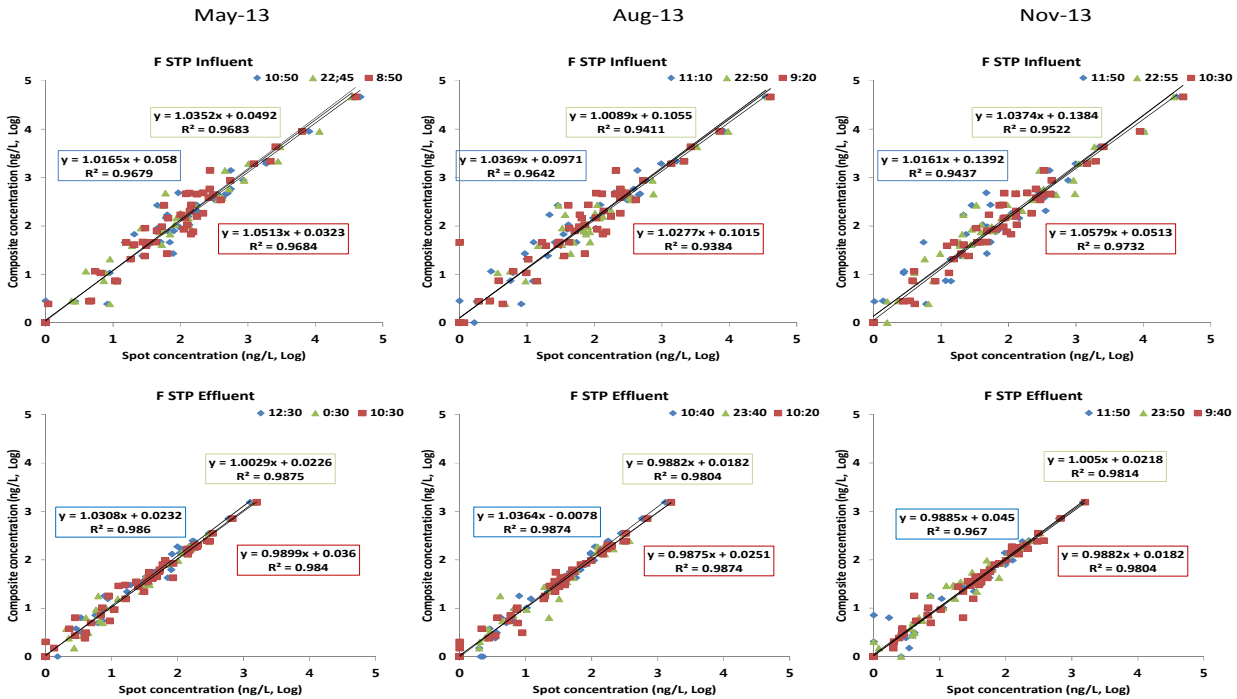

Appendix B. Concentration of PPCPs and estrogens at STPs E and F from 2011 through 2014

	STP E																			
	Concentration (ng/L)																			
	2011		2012								2013								2014	
	3		4		5		6		7		8		9		10		11		12	
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
Acetaminophen	35109.5	6.0	29970.1	5.0	45745.0	10.6	23694.8	6.2	30128.7	16.1	38131.0	189.4	23632.5	19.6	39662.1	16.8	33332.7	N.A.	35194.2	58.8
Caffeine	7439.5	17.5	3677.1	13.9	8586.4	52.7	8141.4	25.4	8008.4	104.4	9829.1	39.9	7958.4	29.9	7011.7	103.4	5260.8	29.9	8963.3	35.3
Ibuprofen	2249.0	N.A.	2206.0	22.2	2679.2	5.7	1501.6	0.0	2416.4	0.0	1863.7	N.A.	1679.5	0.0	2413.8	137.7	2902.4	6.6	1883.7	64.7
Naproxen	1772.0	56.5	762.2	13.2	1766.8	55.9	1693.1	48.7	1696.3	119.4	1703.1	642.9	1991.8	69.6	2853.6	340.0	2217.6	232.7	2945.5	415.4
Theophylline	1227.0	16.5	959.4	7.8	1400.1	41.2	1035.9	25.6	2207.6	39.7	1889.0	27.5	1512.0	34.1	1388.6	161.8	1339.9	31.5	1852.1	29.1
Ciprofloxacin	1204.0	67.0	453.8	45.1	2606.0	137.6	1456.3	127.3	836.1	72.2	587.9	126.0	986.1	93.5	617.5	74.8	1147.6	190.6	1466.9	477.1
Sulpiride	972.5	645.5	750.2	656.1	566.5	773.9	610.2	284.6	523.3	447.9	2379.0	1800.7	994.9	579.8	843.9	471.3	774.2	615.2	1052.3	619.4
Levofloxacin	708.5	168.5	474.7	96.6	1293.8	314.9	463.3	156.5	1173.2	221.2	1498.7	513.2	1266.6	367.6	887.0	319.8	1473.9	495.7	1777.2	930.4
DEET	63.5	31.5	10.5	16.4	66.1	67.8	1104.2	79.0	34.7	21.1	62.7	27.8	696.8	373.9	201.0	273.6	133.0	57.8	48.3	36.1
Clarithromycin	1035.0	576.0	857.9	308.7	446.4	371.2	200.1	99.8	1014.6	429.7	617.3	556.8	435.3	195.0	461.3	180.7	721.9	333.8	576.8	659.0
Bezafibrate	41.5	22.5	25.3	48.7	129.0	7.7	196.2	2.6	177.5	52.9	191.1	155.6	164.6	12.8	756.2	70.3	254.1	49.5	296.8	154.2
Atenolol	676.5	298.0	287.5	170.8	664.3	330.2	414.4	164.4	717.1	381.0	589.0	421.0	614.8	272.1	520.5	385.6	431.5	240.5	727.4	453.0
Mefenamic_acid	173.5	141.5	215.2	45.0	227.9	85.9	186.2	89.8	157.9	73.0	255.8	119.9	289.8	169.6	404.4	334.6	298.2	209.1	181.3	230.3
Sulfamethoxazole	238.0	236.5	72.5	48.9	310.8	322.8	156.8	163.8	675.4	360.8	257.0	206.7	127.4	142.5	107.6	287.9	183.8	254.3	170.2	197.0
Ketoprofen	218.0	3.5	102.8	5.7	304.9	4.0	121.7	3.3	581.2	8.8	207.8	40.8	108.0	8.2	170.1	76.2	128.6	10.7	189.3	35.0
Roxithromycin	535.5	393.0	284.3	177.2	439.7	339.7	217.7	154.0	281.7	307.4	405.3	410.8	242.7	160.4	480.7	195.0	351.5	274.4	765.5	509.3
Furosemide	159.5	50.5	165.2	33.5	292.7	28.8	168.6	10.8	376.7	42.8	200.0	182.5	163.7	38.3	202.8	117.6	180.5	64.1	330.1	164.9
Sulfapyridine	97.5	171.0	94.1	54.6	N.D.	N.D.	68.4	123.3	250.6	162.6	109.2	121.1	64.6	125.4	266.7	183.2	170.8	157.3	162.6	147.0
Triclosan	164.5	N.A.	159.6	N.D.	287.7	N.D.	104.1	N.D.	91.0	N.D.	105.4	N.A.	249.8	28.0	121.6	N.D.	111.6	35.0	63.5	N.D.
Trimethoprim	98.0	27.0	45.0	77.6	200.8	145.8	71.7	11.4	246.6	110.2	122.6	137.7	70.9	78.7	64.7	51.2	56.7	48.5	100.0	169.9
Crotamiton	60.5	126.0	20.9	28.0	64.2	74.9	145.4	153.1	44.1	41.2	68.2	114.0	125.7	98.2	134.5	156.6	138.3	70.6	43.3	47.8
Carbamazepine	161.0	155.0	74.6	59.8	129.7	174.0	96.8	102.1	138.9	110.1	97.0	142.8	94.9	120.0	82.9	98.9	43.5	60.7	113.4	123.6
Triclocarban	143.5	43.5	52.3	10.3	200.2	N.D.	94.6	41.1	44.1	45.0	80.6	17.1	127.6	52.8	N.D.	N.D.	34.5	15.2	N.A.	N.D.
Azithromycin	103.5	69.5	42.5	29.8	60.3	103.8	185.9	N.D.	44.6	77.2	77.0	96.6	45.2	49.2	61.3	38.2	140.0	65.6	87.5	84.0
Oxytetracycline	29.5	5.0	88.1	0.6	19.7	N.D.	95.2	N.D.	0.0	4.4	43.5	4.0	132.5	3.0	N.D.	N.D.	147.8	2.8	35.1	N.D.
Lincomycin	75.0	89.0	63.0	135.9	100.3	68.5	100.0	26.0	32.9	59.7	171.6	89.4	150.9	41.3	101.1	91.5	78.9	88.4	127.5	134.5
Diclofenac	69.5	95.0	37.9	62.0	64.1	129.5	64.4	76.3	101.0	114.0	118.7	178.4	95.2	136.7	103.5	N.D.	89.8	131.9	122.5	171.8
Sulfadimidine	5.0	3.0	0.6	N.D.	1.9	0.6	1.5	1.1	5.3	6.9	2.6	3.5	9.5	7.3	6.6	5.5	0.9	N.D.	0.8	N.D.
Estriol	-	-	N.D.	N.D.	44.9	N.D.	N.D.	N.D.	60.7	N.D.	34.8	N.D.	121.8	0.0	105.8	N.D.	233.5	N.D.	86.5	N.D.
Enrofloxacin	7.5	N.D.	N.D.	N.D.	16.1	N.D.	N.D.	N.D.	11.4	N.D.	10.6	N.D.	53.8	33.5	0.0	N.D.	17.6	4.2	16.8	10.0
Norfloxacin	97.0	0.5	0.0	4.8	58.3	11.1	29.6	1.4	0.0	N.D.	36.5	10.7	216.7	7.2	38.1	7.9	62.0	15.2	18.5	17.0
Diltiazem	78.5	35.0	40.4	20.8	64.5	46.4	85.0	27.6	69.7	52.9	84.6	53.2	61.2	36.6	84.3	44.3	73.2	44.9	79.1	53.0
Tetracycline	79.5	3.5	7.7	0.2	15.0	0.4	20.1	N.D.	30.9	N.D.	62.2	4.9	0.0	1.6	27.6	3.5	102.9	0.0	14.6	4.5
Erythromycin	N.D.	N.D.	49.5	28.9	40.7	21.2	N.D.	N.D.	64.0	42.2	52.8	63.2	0.0	25.1	0.0	0.0	0.0	62.2	97.3	57.7
ErythromycinN.D.H2O	58.5	40.0	31.6	18.1	37.6	38.6	25.0	N.D.	30.6	31.3	35.3	41.0	23.5	21.0	43.8	22.7	52.6	47.1	71.5	39.9
Propranolol	26.5	28.0	12.9	11.3	22.8	29.4	13.2	20.5	22.6	40.3	18.2	40.9	41.9	48.5	30.6	51.2	25.9	40.5	30.2	53.1
Fenoprofen	10.0	N.D.	14.4	2.6	47.8	N.D.	N.D.	N.D.	20.3	0.0	10.4	N.D.	N.D.	N.D.	N.D.	N.D.	12.2	N.D.	19.9	N.D.
Chlortetracycline	N.D.	N.D.	N.D.	N.D.	1.0	0.7	N.D.	N.D.	0.0	0.0	31.9	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Estrone	-	-	5.2	N.D.	8.6	0.0	29.8	0.1	20.1	1.7	19.3	0.6	21.9	1.0	8.6	0.6	10.1	0.7	2.1	0.4
Antipyrine	12.5	17.0	5.9	7.3	13.4	13.1	18.1	12.8	8.4	13.8	16.0	12.2	9.8	12.3	17.7	13.0	8.5	N.D.	9.4	11.2
Tiamulin	N.A.	0.0	0.5	N.D.	0.6	0.2	N.D.	N.D.	3.3	3.6	0.9	0.8	0.6	0.1	N.D.	0.1	0.0	0.1	1.6	0.1
Indometacin	7.0	9.0	4.6	3.4	8.3	4.8	4.1	1.3	17.7	7.5	10.1	11.7	5.3	3.6	4.6	N.D.	12.2	4.2	8.7	9.8
Estradiol	-	-	N.D.	N.D.	1.0	N.D.	N.D.	0.7	17.4	0.0	2.6	0.0	3.7	N.D.	9.5	N.D.	26.8	N.D.	5.5	N.D.
Primidone	N.A.	3.5	3.5	0.7	5.4	5.5	5.4	2.2	10.2	14.3	14.5	11.3	4.4	13.7	2.7	10.1	3.6	17.1	7.9	15.2
Salbutamol	3.0	N.D.	2.8	N.D.	N.D.	N.D.	N.D.	N.D.	12.9	N.D.	N.D.	5.3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	5.1	N.D.
Metoprolol	0.0	2.5	1.9	0.8	4.8	2.1	4.0	0.7	10.4	4.3	3.9	3.2	5.2	2.0	0.0	3.3	3.7	3.9	6.1	5.3
Griseofulvin	N.D.	N.D.	2.1	2.3	11.1	0.3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	6.4	5.2	N.D.	N.D.	N.D.	N.D.	4.8	N.D.
Ethenzamide	N.A.	1.0	0.6	2.4	0.0	3.7	0.6	N.D.	3.5	10.8	10.3	8.6	0.7	3.1	0.7	2.5	1.4	2.8	3.8	2.6
Tylosin	6.0	4.0	4.1	3.2	2.7	3.2	N.D.	N.D.	9.5	4.9	3.8	2.8	N.D.	0.9	3.6	1.8	0.0	1.7	1.4	4.0
2QCA	N.A.	10.5	N.A.	1.9	N.D.	N.D.	N.D.	N.D.	N.A.	12.6	N.A.	20.1	11.8	10.8	N.A.	10.5	26.3	6.6	24.4	6.9
Isopropylantipyrine	2.5	4.5	3.7	3.9	2.0	12.6	1.7	5.5	2.2	7.7	14.8	15.2	6.2	8.0	2.8	4.3	4.3	10.2	5.1	3.8
Sulfadimethoxine	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1.0	0.0	0.0	0.4	1.0	0.1	0.9	0.3	2.3	0.0
Pirenzepine	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Disopyramide	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.5	N.D.	N.D.	N.D.	0.3	0.2	4.7	1.8
Dipyridamole	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Clofibric_acid	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.0	1.3	N.D.	N.D.
Sulfathiazole	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	6.5	1.1	N.D.	N.D.
Sulfamerazine	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Nalidixic_acid	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1.2	N.D.
Sulfamonomethoxine	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Ceftiofur	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Clenbuterol	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Ifenprodil	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Thiamphenicol	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Ethynylestradiol	-	-	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

(Continue)

STP F																					
Concentration (ng/L)																					
2011		2012										2013								2014	
Fall		Winter		Srping		Summer		Fall		Winter		Srping		Summer		Fall				Winter	
Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
70341.0	16.0	15832.0	20.3	61880.8	15.4	32275.1	N.A.	48477.6	55.3	46436.6	55.3	46575.2	32.0	60236.6	28.1	69235.1	N.A.	67126.1	115.5		
5510.5	31.5	3965.4	12.7	6297.0	24.5	6436.2	108.3	5614.2	43.8	8938.2	29.0	5714.8	37.1	6264.6	99.4	4289.6	191.4	6317.8	54.9		
3848.0	22.0	1633.7	6.7	3917.3	8.5	2253.0	25.9	3050.7	25.4	4310.5	30.2	4033.6	16.2	5058.0	N.A.	4628.1	24.2	3496.8	77.4		
3063.5	25.5	813.7	99.4	2292.9	127.9	1677.1	181.7	2254.2	162.1	1939.1	97.6	2538.8	72.2	1934.9	126.1	3439.1	201.4	2678.1	519.1		
2153.0	29.5	811.0	8.7	2559.0	23.1	2060.6	60.5	2644.1	53.3	2162.4	35.0	2820.1	30.7	2317.0	60.1	2505.6	100.3	2450.3	58.9		
461.5	10.5	155.7	10.1	737.8	184.7	1382.9	18.0	315.1	15.2	272.8	15.7	567.3	6.2	521.6	9.5	353.1	400.4	360.5	15.0		
807.5	392.0	543.9	513.5	1113.7	661.2	649.4	254.3	747.2	314.5	1397.9	1553.6	1623.4	497.5	1164.6	493.4	1203.3	563.7	1197.8	672.0		
281.0	6.5	184.4	15.9	634.3	338.6	1124.3	32.3	602.1	36.1	580.3	44.7	1150.6	25.4	609.5	39.1	539.8	90.6	741.1	30.0		
85.0	53.0	22.6	14.8	69.3	77.0	356.0	637.5	43.8	67.1	46.0	42.8	295.2	520.2	307.1	455.2	139.7	104.6	25.8	44.8		
899.5	324.0	566.4	337.7	569.1	338.5	292.4	115.7	755.0	389.9	870.8	713.5	392.1	232.2	511.5	281.0	972.7	460.4	1216.7	1075.8		
437.5	59.0	204.2	107.9	329.6	76.7	427.5	50.8	199.2	200.5	461.0	239.2	218.0	27.3	238.1	38.9	257.9	155.3	343.5	443.2		
736.0	71.5	322.7	31.0	752.9	49.4	622.3	N.A.	823.2	126.5	441.2	168.4	680.1	85.8	586.3	83.4	583.6	104.2	520.6	109.4		
408.5	151.0	135.1	114.4	483.9	212.2	483.8	168.9	552.1	296.6	476.0	199.5	703.9	257.0	871.0	300.0	1031.4	360.4	646.6	349.5		
224.5	149.5	105.9	48.4	532.7	150.3	284.3	179.5	1779.6	1257.0	343.9	205.2	482.9	140.5	367.5	146.6	662.1	181.2	481.7	109.5		
155.5	65.5	82.0	20.6	215.4	59.5	154.6	46.5	217.7	144.1	204.9	131.5	229.7	64.2	165.7	70.4	250.4	136.6	184.9	145.9		
360.5	234.5	338.0	267.1	433.7	285.4	206.5	109.6	500.0	310.7	383.8	355.8	285.9	173.9	222.5	180.3	234.8	297.5	518.0	369.9		
247.0	226.0	192.2	46.8	440.7	147.3	308.0	131.8	349.0	194.9	453.7	249.1	462.1	189.2	458.7	140.8	365.1	242.5	786.7	318.0		
200.5	113.5	74.0	42.9	N.A.	N.A.	346.2	117.8	167.8	226.3	182.4	79.8	293.1	115.8	202.9	112.0	562.2	137.6	331.3	187.6		
N.A.	N.A.	N.A.	24.8	291.9	N.A.	147.3	86.0	113.0	N.A.	252.0	N.A.	145.8	79.8	N.D.	N.D.	N.D.	128.4	N.D.	N.A.		
103.0	35.5	63.7	75.5	211.7	93.1	99.5	59.0	117.9	93.2	95.8	84.6	277.8	95.4	126.0	76.9	138.3	84.3	189.1	171.7		
43.5	79.5	21.9	23.3	92.8	70.8	170.6	218.0	42.0	57.8	46.3	62.6	231.7	142.0	164.2	159.5	136.6	87.1	24.3	65.8		
222.0	230.5	97.1	98.6	264.5	249.3	252.9	166.5	172.9	148.5	156.5	154.7	208.6	143.9	138.8	116.8	65.6	65.1	232.5	188.8		
62.0	N.D.	6.0	8.4	105.1	N.A.	100.2	78.1	54.8	37.8	216.6	N.A.	59.4	51.3	N.A.	N.D.	N.A.	27.2	N.D.	N.D.		
65.0	26.5	114.4	78.6	104.6	150.0	N.A.	56.0	91.1	139.8	144.5	138.6	48.6	57.7	88.6	96.8	63.0	88.3	125.4	124.3		
27.0	N.D.	8.1	0.0	12.4	N.D.	58.0	1.6	43.1	N.D.	45.8	2.0	204.7	N.D.	85.6	N.A.	234.3	21.1	80.6	N.D.		
423.5	203.5	278.1	224.7	584.3	145.5	144.1	89.7	92.3	168.5	265.9	187.6	63.7	68.3	136.6	119.4	285.6	170.4	323.4	274.0		
139.5	128.0	43.2	79.4	174.1	135.6	106.0	105.4	172.5	190.6	148.0	181.5	164.6	171.2	133.5	155.0	148.8	152.2	99.4	189.2		
17.5	16.5	7.5	9.6	48.5	35.4	246.9	157.8	1511.0	1971.1	75.4	42.0	125.8	119.9	65.6	40.4	17.7	9.7	12.0	6.4		
-	-	N.D.	N.D.	53.4	N.D.	N.D.	N.D.	64.0	N.D.	56.3	N.D.	113.0	0.0	116.6	N.D.	254.1	N.D.	104.7	N.D.		
N.D.	N.D.	N.D.	0.5	N.D.	N.D.	N.D.	N.D.	0.0	5.9	170.1	6.4	102.2	31.2	N.D.	N.D.	41.0	437.2	66.8	N.D.		
17.5	N.D.	N.D.	N.D.	88.5	9.0	71.9	N.D.	N.D.	N.D.	N.D.	N.D.	74.5	N.D.	20.2	N.D.	0.0	270.4	N.D.	N.D.		
95.5	28.5	36.7	18.6	114.8	49.4	122.6	36.9	101.9	51.9	78.8	56.7	87.3	39.4	101.6	45.7	107.7	48.8	94.4	61.2		
69.5	N.D.	61.6	1.0	30.9	0.5	N.A.	1.1	57.0	N.D.	90.0	1.5	14.7	0.0	202.5	N.D.	32.2	40.4	76.2	2.5		
N.D.	N.D.	28.4	N.D.	103.0	31.2	N.D.	N.D.	79.4	N.D.	N.A.	42.8	0.0	34.5	N.D.	N.D.	N.D.	N.D.	N.D.	39.3		
50.0	33.5	24.0	16.2	50.2	42.3	19.5	12.0	40.0	31.1	216.6	40.6	37.8	22.9	29.7	18.9	71.6	52.4	32.8	29.1		
33.5	31.0	9.8	16.5	47.9	29.1	24.4	22.6	29.4	45.1	24.0	45.6	49.8	32.5	50.8	40.2	31.7	42.0	32.6	42.8		
18.0	N.D.	20.9	3.6	43.3	N.D.	N.D.	N.D.	27.8	N.D.	20.6	N.D.	N.D.	N.D.	N.D.	N.D.	29.7	N.D.	38.5	N.D.		
43.5	N.D.	2.9	1.1	5.7	0.4	N.D.	N.D.	33.0	N.D.	483.8	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	76.0	312.8	N.D.		
-	-	5.6	0.5	10.8	0.9	52.4	3.8	22.1	3.8	16.0	1.5	51.4	3.8	20.9	4.6	14.8	27.5	5.6	6.3		
33.5	22.0	13.0	14.7	41.6	36.6	43.3	38.0	27.1	36.6	38.9	27.7	21.3	20.1	49.8	35.7	71.2	33.4	36.8	28.4		
13.0	19.0	14.9	21.7	7.5	9.4	17.8	18.5	57.9	149.6	67.5	34.8	17.9	23.3	0.0	4.3	17.9	19.4	124.6	112.5		
13.0	5.0	5.3	3.9	7.1	5.4	5.4	4.6	8.8	10.2	0.0	17.9	10.3	5.2	N.D.	N.D.	N.D.	10.0	13.6	N.D.		
-	-	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	28.9	N.D.	N.D.	N.D.	15.3	N.D.	N.D.	N.D.	12.9	N.D.	N.D.	N.D.		
N.D.	N.D.	0.9	N.D.	0.8	N.D.	N.D.	N.D.	18.9	7.0	46.1	22.1	10.1	22.6	30.2	21.7	104.5	17.3	38.3	27.6		
3.5	N.D.	4.3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	10.8	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	4.7	N.D.		
9.0	3.5	4.4	1.8	5.2	6.2	2.9	3.2	9.6	7.9	7.4	5.5	12.2	3.4	6.1	2.6	4.9	5.6	6.7	6.2		
N.D.	N.D.	2.9	N.A.	6.7	4.0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	9.9	7.0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.		
N.D.	N.D.	0.3	4.3	N.D.	3.8	N.D.	N.D.	4.3	5.9	2.5	2.4	1.5	4.5	3.0	1.3	1.1	1.8	6.3	6.1		
N.D.	6.0	9.0	7.2	2.4	5.8	N.D.	N.D.	11.2	9.0	7.2	7.2	4.2	2.9	8.8	1.9	11.8	4.1	17.5	8.3		
N.D.	N.D.	20.4	4.9	16.9	11.9	N.D.	N.D.	24.5	39.8	14.6	31.9	N.A.	16.7	N.A.	18.7	0.0	8.0	N.D.	10.2		
4.5	6.0	4.3	6.3	33.3	19.9	6.5	10.6	5.2	8.1	10.7	10.2	4.8	10.1	4.3	6.7	4.8	4.4	7.9	9.0		
N.D.	N.D.	N.D.	N.D.	0.3	0.4	N.D.	N.D.	0.4	N.D.	11.5	3.8	5.7	3.1	26.4	8.4	33.8	8.2	21.8	4.8		
N.D.	N.D.	N.D.	0.3	1.0	N.D.	N.D.	N.D.	4.0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.		
N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	3.4	3.3	N.D.	0.1	N.D.	N.D.	N.D.	N.D.	0.4	0.4	8.3	0.5		
6.5	N.D.	2.2	1.6	3.4	N.D.	N.D.	N.D.	24.7	3.7	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.0	20.9	13.5	N.D.		
7.0	3.0	N.D.	0.8	N.D.	5.6	N.D.	0.9	5.1	6.9	N.D.	2.7	N.D.	N.D.	N.D.	N.D.	26.9	8.8	6.8	3.4		
32.5	28.0	8.4	7.6	49.5	55.9	225.6	105.1	226.3	229.4	85.5	36.0	48.9	35.0	129.4	58.7	56.4	28.7	2794.7	741.7		
N.D.	N.D.	N.D.	2.1	N.D.	N.D.	N.D.	N.D.	1.3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	3.3	N.D.	0.6		
N.D.	N.D.	N.D.	1.8	N.D.	N.D.	N.D.	3.9	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	6.7	6.4	0.0		
N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.		
N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.		
N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.		
N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.		
N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.		
-	-	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.		

Appendix C. Seasonal loading of PPCPs and estrogens detected at each point

Gyeongan River

River loading (g/day)

	Nov-11							Jan-12							May-12							Aug-12							Nov-12						
Compounds	s1	s2	s3	s4	s5	s7	s6	s1	s2	s3	s4	s5	s7	s6	s1	s2	s3	s4	s5	s7	s6	s1	s2	s3	s4	s5	s7	s6	s1	s2	s3	s4	s5	s7	s6
2QCA	0.82	1.61	-	-	-	-	0.72	0.04	0.47	0.34	0.31	0.18	0.37	0.20	2.06	-	2.51	2.86	1.60	4.64	1.33	-	-	-	-	-	-	-	2.43	2.91	3.98	3.11	-	4.96	1.72
Acetaminophen	28.30	20.81	21.67	16.49	26.59	31.75	7.39	48.15	53.15	51.83	21.30	20.89	25.76	11.47	5.92	24.77	7.17	5.58	37.59	18.00	1.99	13.43	15.08	4.59	1.61	6.31	22.29	0.60	73.80	22.81	60.23	53.21	55.45	74.31	31.53
Antipyrine	-	0.86	1.72	2.49	1.09	2.75	0.48	0.25	0.69	0.80	0.50	0.74	0.86	0.15	-	2.74	2.73	3.86	2.04	4.89	1.85	-	1.85	1.58	1.45	2.72	3.37	-	-	-	-	-	-	-	-
Atenolol	-	7.94	5.26	4.51	5.44	16.25	2.49	0.99	3.13	3.63	1.78	1.81	8.19	0.86	-	4.95	3.27	1.83	1.70	-	-	-	-	-	-	-	-	-	3.33	14.90	10.37	9.63	8.04	18.25	3.29
Azithromycin	0.46	1.18	1.29	1.24	0.78	2.50	1.12	0.54	2.73	1.65	0.92	0.90	3.49	1.00	-	1.06	0.74	0.22	0.29	0.64	0.13	0.52	0.94	0.40	0.18	-	-	-	1.01	2.62	2.14	1.37	1.32	1.52	0.91
Bezafibrate	2.83	5.36	3.86	4.35	4.35	5.00	0.16	2.23	8.75	6.13	3.40	3.58	6.41	0.46	2.69	6.41	5.63	2.90	2.42	2.78	0.56	0.16	3.80	2.07	1.03	0.53	0.94	0.02	2.90	4.83	8.78	6.65	5.71	8.37	1.12
Caffeine	38.61	22.31	19.41	27.53	31.10	37.25	7.23	26.08	21.52	18.54	10.43	9.90	15.89	6.21	61.77	35.99	36.20	26.45	40.05	44.90	10.36	34.28	31.73	37.23	23.37	29.67	40.86	2.45	111.51	35.17	48.96	52.03	56.44	76.92	16.97
Carbamazepine	5.93	17.38	16.30	19.75	19.28	32.00	8.68	1.43	6.53	5.94	4.22	4.29	9.83	3.22	4.04	18.29	20.02	14.62	15.11	37.35	11.31	2.01	11.64	9.73	9.02	9.12	13.53	1.03	3.90	8.34	10.94	8.42	7.74	16.58	4.18
Ceftiofur	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Chlortetracycline	-	8.90	-	-	-	-	-	-	0.89	-	-	-	-	-	-	-	-	-	-	-	-	-	0.19	-	-	-	-	-	-	-	-	-	-	-	-	-
Ciprofloxacin	0.91	1.72	1.50	0.00	1.40	3.50	-	0.27	0.84	0.44	0.53	0.20	0.81	0.28	-	0.20	0.03	-	0.30	4.13	0.05	1.89	3.38	1.82	2.77	3.67	3.32	0.27	1.90	1.91	1.80	1.53	1.45	2.58	1.67
Clarithromycin	3.74	20.59	22.10	22.39	18.82	47.74	11.97	2.32	18.91	16.15	9.49	9.82	29.30	10.99	3.25	22.46	19.70	12.58	9.91	28.22	8.32	0.75	7.19	4.46	2.12	0.00	3.95	-	5.34	24.55	27.18	20.66	17.84	23.10	14.07
Clenbuterol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Clofibric_acid	-	-	-	-	-	-	0.16	0.09	0.12	0.11	0.12	0.10	0.21	-	0.13	0.30	0.36	0.39	0.35	0.23	-	-	0.20	0.12	-	-	-	-	1.00	1.08	-	-	1.11	1.80	-
Crotamiton	2.92	7.94	7.62	9.18	9.02	16.00	4.42	0.77	2.04	2.15	1.48	1.52	7.19	5.22	1.40	7.23	7.04	5.74	5.58	16.27	12.32	2.99	15.34	13.56	11.23	11.28	16.98	2.18	3.41	5.60	6.63	5.04	4.79	7.88	2.49
DEET	3.29	6.22	6.44	7.78	6.53	10.50	1.53	0.46	2.51	1.52	0.88	0.88	2.70	0.50	2.07	6.40	8.53	5.69	4.96	10.21	6.14	8.82	53.20	36.88	33.38	33.01	40.53	5.05	2.81	5.65	6.46	5.42	4.93	11.88	2.53
Diclofenac	0.27	6.65	2.90	2.49	2.33	4.00	1.04	0.06	3.21	1.85	1.06	1.05	3.15	0.93	-	0.67	0.76	0.32	0.44	1.17	1.16	-	1.34	0.23	-	-	-	-	1.76	4.20	5.19	5.28	9.59	10.47	5.28
Diltiazem	0.37	1.82	1.50	1.40	1.40	2.75	0.48	0.19	1.06	0.76	0.41	0.40	1.36	0.27	0.11	1.39	0.55	0.35	0.33	1.76	0.62	0.10	1.64	0.40	0.11	0.09	0.68	0.06	1.68	2.42	3.59	2.69	2.62	4.26	1.55
Dipyridamole	-	-	-	-	-	-	-	0.21	-	-	-	-	-	0.20	-	0.40	0.35	0.00	0.37	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Disopyramide	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.09	-	-	0.99	1.01	-	0.72
Enrofloxacin	-	-	-	-	-	-	0.08	0.09	-	0.06	0.04	-	-	0.09	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Erythromycin	-	-	-	7.62	-	-	1.21	0.00	1.58	1.70	1.27	1.31	2.44	1.52	-	6.21	0.00	0.00	4.53	9.58	3.82	1.99	1.55	0.99	1.21	-	4.76	-	8.45	8.20	41.29	15.79	10.78	4.74	1.97
Erythromycin-H2O	0.82	2.36	2.79	2.95	3.11	5.25	0.80	0.18	1.06	1.26	0.87	0.90	2.20	0.88	-	3.04	2.89	2.09	1.81	4.02	2.05	0.27	0.93	0.54	0.38	-	1.55	-	7.08	5.21	33.65	14.83	9.99	5.67	1.28
Estradiol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.18	0.54	-	-	-	-	0.02	-	-	-	-	-	-	-
Estriol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Estrone	-	-	-	-	-	-	-	0.03	0.05	0.10	0.03	0.03	0.05	0.01	0.25	0.49	0.31	0.33	0.35	0.79	0.32	0.14	0.18	-	0.14	0.20	-	0.03	0.57	0.34	0.34	0.55	0.18	0.42	0.26
Ethenzamide	-	-	-	-	-	-	-	-	0.17	0.25	0.19	0.17	0.36	0.28	-	0.10	-	-	-	-	-	-	-	-	-	-	-	-	0.52	0.83	0.88	0.66	0.67	1.13	0.33
Ethynylestradiol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Fenoprofen	-	-	-	-	-	-	0.24	0.66	0.52	0.46	-	0.31	-	-	-	-	-	-	-	2.05	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Furosemide	-	7.19	-	-	-	1.00	-	-	0.92	0.19	-	-	0.54	0.17	-	-	-	-	-	-	-	-	-	-	0.75	-	0.41	-	1.21	3.03	2.23	2.07	-	4.23	0.94
Griseofulvin	-	0.00	-	-	-	0.00	-	-	-	-	-	-	-	-	-	-	-	0.01	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ibuprofen	10.68	8.26	5.79	6.22	10.89	11.25	-	8.43	8.28	7.71	3.69	3.21	6.56	1.49	7.32	15.29	8.35	3.95	9.25	6.53	2.73	1.94	5.44	4.36	1.81	-	3.61	-	10.39	3.34	13.26	7.53	9.77	15.18	6.67
Ifenprodil	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Indometacin	0.27	0.75	0.43	0.47	-	0.75	0.16	0.25	0.38	0.37	-	0.32	0.60	0.25	-	0.63	-	-	-	-	0.94	-	-	-	-	-	-	-	-	2.09	-	-	-	-	-
Isopropylantipyrine	0.09	0.86	0.75	1.24	0.93	1.00	0.08	-	0.48	0.42	0.44	0.27	0.44	0.02	-	6.04	1.38	1.15	0.82	1.75	0.54	0.25	1.17	1.39	1.27	1.45	1.18	0.04	0.09	0.38	1.05	1.16	1.01	1.41	0.20
Ketoprofen	-	0.64	-	-	-	-	-	0.11	0.16	0.13	-	0.10	0.24	-	-	-	-	-	-	-	-	0.07	-	-	-	-	0.02	-	-	-	-	-	-	-	-
Levofloxacin	0.64	2.36	1.50	0.93	2.02	4.75	0.64	0.45	1.34	0.93	0.70	0.67	3.00	0.61	-	1.20	0.80	0.26	0.95	4.13	0.00	1.71	4.74	1.49	1.86	1.76	2.64	0.22	2.32	6.27	4.77	3.07	2.88	2.27	1.70
Lincomycin	1.46	9.55	13.94	16.17	15.40	17.50	1.29	1.50	23.02	11.03	5.79	5.87	18.96	7.59	-	8.91	8.49	4.28	2.76	7.42	4.17	0.00	6.32	3.44	1.76	0.29	2.03	0.17	-	3.87	6.47	3.10	1.67	6.39	0.18
Mefenamic_acid	2.56	12.44	10.40	11.35	11.35	17.50	1.93	0.96	6.84	5.95	3.94	3.68	6.44	1.24	1.42	9.88	7.33	5.89	5.89	12.91	9.18	0.99	7.59	3.52	1.81	0.00	5.30	1.22	3.50	10.47	14.03	11.56	11.20	15.48	-
Metoprolol	-	-	-	-	-	-	-	0.02	0.10	0.10	0.06	0.05	0.22	0.02	-	0.32	0.19	0.21	0.10	0.45	0.34	0.01	0.08	0.02	-	-	-	0.02	0.63	0.91	0.72	0.33	0.70	0.99	-
Nalidixic_acid	-	-	-	-	-	-	-	0.14	0.24	0.20	0.20	0.18	0.38	0.20	-	-	-	-	-	-	-	0.76	0.45	-	0.86	-	-	-	-	-	-	-	-	-	-
Naproxen	5.75	6.76	5.79	6.22	7.15	12.00	3.54	3.48	9.45	8.01	4.44	4.16	5.75	1.05	4.18	9.20	7.52	4.64	6.95	9.16	6.04	3.03	13.91	6.47	3.02	3.15	6.55	1.01	12.15	22.92	17.37	15.92	14.39	21.51	4.59
Norfloxacin	-	-	-	-	-	-	-	-	0.55	-	0.41	-	-	0.32	-	-	-	-	-	0.48	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Oxytetracycline	-	27.78	-	-	5.29	2.00	-	-	0.15	-	-	0.03	-	0.05	-	-	-	-	-	0.34	-	-	-	-	-	-	-	-	5.36	-	-	-	1.43	-	-
Pirenzepine	-	-	-	-	-	-	-	0.03	0.03	0.05	0.04	0.04	0.07	0.02	-	-	-	-	-	-	-	-	-	-	-	0.16	-	-	-	-	-	-	0.90	-	0.60
Primidone	-	-	-	-	-	0.25	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.43	-	-	3.30	-
Propranolol	-	1.50	0.97	0.62	0.62	1.75	-	-	0.66	0.55	0.31	0.27	0.75	0.31	0.09	0.80	0.58	0.27	0.02	0.87	0.44	-	0.89	0.29	0.02	-	0.22	0.04	0.74	2.15	2.49	1.98	1.91	2.91	1.12
Roxithromycin	2.56	16.09	14.80	16.02	11.66	31.75	5.30	1.53	12.58	11.74	6.68	7.08	18.07	4.73	1.83	17.69	16.17	10.69	9.85	25.15	4.89	0.74	6.56	3.37	2.17	-	5.31	-	3.44	12.69	18.79	13.92	12.19	13.37	4.49
Salbutamol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sulfadimethoxine	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.06	0.07	0.11	0.14	-	-	-	-	-	-	-	-	0.08	-	-	-	-	-	-
Sulfadimidine	0.37	1.93	1.93	2.33	2.02	2.75	0.16	0.13	1.01	0.77	0.62	0.60	0.86	0.07	0.66	3.72	3.38	2.44	2.08	2.21	0.29	0.17	10.64	4.18	2.74	3.42	2.61	0.06	1.76	10.09	54.78	37.52	34.78	38.87	0.69
Sulfamerazine	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.28	-	0.07	-	-	-	-
Sulfamethoxazole	2.74	14.05	14.69	18.20	17.73	33.00	6.35	1.23	5.66	5.02	3.75	4.09	9.21	2.00	7.25	20.57	19.37	15.66	14.36	31.87	8.01	0.92	15.64	10.16	8.81	10.10	13.26	1.10	4.85	8.93	45.84	33.75	32.12	43.91	3.32
Sulfamonomethoxine	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.14	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sulfapyridine	6.75	12.01	9.01	10.58	9.33	17.75	3.54	1.44	3.37	3.53	2.32	2.19	6.04	1.30	-	-	-	-	-	-	-	0.46	5.79	2.84	1.43	1.71	4.21	0.49	15.76	9.41	13.30	12.02	11.46	18.30	2.43
Sulfathiazole	0.27	2.68	2.15	1.87	2.64	2.50	0.64	0.05	0.82	0.49	0.36	0.31	0.39	0.09	0.63	2.28	1.96	1.68	1.31	1.27	1.19	-	7.48	2.21	1.31	1.02	0.88	0.14	1.43	2.53	6.80	4.93	4.39	4.79	0.99
Sulpiride	5.29	40.97	34.86	46.03	45.72	90.24	21.78	5.44	36.98	37.42	25.21	25.44	79.75	27.75	-	63.44	62.20	43.19	41.09	98.59	48.76	1.89	29.34	25.44	19.98	6.63	20.69	1.74	6.30	26.62	31.13	23.89	21.68	41.03	9.48
Tetracycline	-	1.72	-	-	0.62	-	-	-	0.17	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Theophylline	5.66	6.11	6.22	7.00	8.40	10.75	1.69	1.86	4.42	3.84	2.42	2.37	4.56	1.71	6.16	10.26	8.91	7.58	10.04	14.40	4.71	3.29	10.37	9.20	6.91	7.55	9.79	1.08	11.99	10.31	11.16	12.54	12.60	18.13	6.66
Thiamphenicol	-	-	-	-	-	-	-	-	-	-	-	0.84	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Tiamulin	0.00	1.29	0.64	0.62	0.31	0.25	-	0.08	1.19	0.77	0.42	0.39	0.59	0.06	0.05	0.33	0.18	0.14	0.10	0.17	0.06	0.01	0.64	0.16	0.07	0.03	0.05	-	1.14	1.85	3.79	2.90	2.32	3.32	0.72
Triclocarban	3.74	5.26	7.40	-	-	8.75	4.90	0.66	1.16	0.79	0.99	0.48	1.41	0.58	2.42	2.43	1.22	1.30	2.39	4.34	2.21	2.12	4.53	2.30	2.43	-	4.07	-	4.71	-	8.16	5.38	4.25	-	-
Triclosan	-	-	-	-	-	-	-	-	-	1.12	0.00	0.81	-	-	-	-	-	-	-	-	-	4.38	3.08	2.13	6.02	-	-	-	-	-	-	-	-	-	-
Trimethoprim	-	1.18	0.75	0.16	0.31	-	-	0.35	3.46	2.45	1.50	1.61	5.36	1.87	-	4.15	4.16	2.32	2.15	7.28	3.36	-	3.55	1.66	1.41	1.08	1.76	0.25	1.93	2.41	5.45	3.52	2.99	5.59	1.89
Tylosin	-	-	-	-	0.78	1.50	-	0.30	0.60	0.41	0.31	0.34	0.70	0.24	0.47	-	-	-	-	-	-	-	-	-	-	-	0.96	0.00	1.37	-	1.62	1.31	1.28	-	-

(Table continue)

	Gyeongan River River loading (g/day)																																				
	Feb-13							May-13							Aug-13							Nov-13							Jan-14										
Compounds	s1	s2	s3	s4	s5	s7	s6	s1	s2	s3	s4	s5	s7	s6	s1	s2	s3	s4	s5	s7	s6	s1	s2	s3	s4	s5	s7	s6	s1	s2	s3	s4	s5	s7	s6		
2QCA	1.41	2.52	4.27	2.06	1.27	3.63	0.90	1.56	3.94	4.33	4.76	3.08	6.14	2.47	-	-	-	-	-	-	-	0.78	1.04	1.71	2.48	2.31	6.30	1.29	0.29	1.22	0.93	0.93	1.26	3.48	3.37		
Acetaminophen	169.16	107.99	203.71	83.45	87.49	198.82	35.35	21.62	24.92	25.49	12.73	20.31	34.22	58.69	68.34	79.95	72.16	54.34	63.25	107.07	37.92	47.60	8.27	26.48	90.38	51.81	95.37	31.04	111.18	44.97	74.08	91.00	124.14	241.61	134.62		
Antipyrine	-	0.69	1.61	-	-	-	-	-	2.91	1.99	3.40	2.67	-	-	-	2.05	2.50	6.12	2.08	6.60	-	-	-	3.17	3.86	4.22	4.88	1.28	-	1.98	1.58	1.65	1.46	4.05	2.26		
Atenolol	-	11.54	12.80	4.77	4.87	13.94	2.72	0.71	9.31	6.01	3.27	3.54	14.11	4.77	-	5.94	5.87	8.74	7.81	16.92	-	0.85	9.13	9.28	-	9.74	-	-	1.38	8.78	7.90	6.01	6.53	35.68	20.05		
Azithromycin	0.56	1.89	1.88	1.22	0.78	1.71	0.89	0.52	1.62	0.82	0.67	0.80	1.82	1.00	0.31	1.92	0.86	1.53	0.66	1.59	0.98	0.37	3.10	0.94	0.87	1.12	4.86	4.64	0.31	6.27	2.96	2.82	2.80	8.98	9.84		
Bezafibrate	3.90	13.02	14.56	6.78	6.22	14.31	3.36	0.97	5.60	2.71	1.85	1.94	3.66	1.09	1.28	2.40	2.86	2.56	2.27	5.22	1.25	1.90	2.20	7.97	9.66	9.07	21.06	1.71	4.24	17.03	17.42	13.22	12.75	28.03	7.93		
Caffeine	114.17	72.43	76.65	34.96	39.09	89.04	26.95	44.30	37.68	36.21	35.38	37.84	65.19	39.50	37.20	33.55	27.35	46.21	55.64	97.28	25.74	49.13	20.20	41.10	66.67	60.50	121.44	67.31	63.92	34.03	30.30	34.49	44.76	91.92	60.70		
Carbamazepine	3.78	10.99	11.57	5.22	5.02	11.99	3.13	3.93	14.55	15.48	13.76	14.23	27.49	6.25	2.64	10.04	9.89	15.19	15.93	24.57	5.21	3.63	11.58	13.50	19.42	20.79	52.97	19.57	3.31	12.93	13.05	10.52	10.85	28.85	28.75		
Ceftiofur	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.11	-	-	-	-	-	-		
Chlortetracycline	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	4.59	1.36	-	-	-	-	-	-	-	-	-	-		
Ciprofloxacin	0.74	1.94	2.82	1.06	0.52	3.29	0.73	1.36	4.02	2.09	1.90	1.85	7.43	1.76	1.30	0.50	2.00	1.96	0.73	1.36	3.18	0.90	1.25	8.02	2.65	6.08	5.56	2.00	0.75	1.50	1.33	0.78	0.63	4.41	3.76		
Clarithromycin	6.35	35.95	33.72	11.25	11.16	29.05	9.86	4.49	19.08	17.40	12.45	12.67	23.50	7.52	2.64	15.61	13.46	19.78	15.05	28.92	7.19	5.41	31.66	37.78	42.45	38.88	100.89	40.68	7.05	56.97	45.75	35.32	36.74	110.54	91.65		
Clenbuterol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.06	0.14	0.18	-	-		
Clofibric_acid	-	0.23	0.20	0.11	0.13	0.24	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.25	0.39	0.52	0.56	1.54	0.17	0.03	0.29	0.22	0.15	0.12	0.23	0.26		
Crotamiton	1.80	6.71	5.92	2.22	2.29	6.00	2.70	2.34	12.69	13.84	12.49	11.07	24.15	6.66	41.13	24.49	29.45	74.18	49.42	56.13	18.97	7.66	13.93	17.79	22.92	30.34	52.93	25.22	2.98	5.12	5.38	4.02	4.15	12.98	12.47		
DEET	0.86	3.86	4.33	1.95	1.70	3.66	0.85	12.54	45.33	47.02	41.04	37.88	83.31	25.74	9.11	47.12	40.34	67.45	62.26	89.29	7.78	7.58	11.24	16.14	23.18	29.80	50.71	20.03	1.60	3.67	4.23	3.50	3.45	8.98	7.07		
Diclofenac	1.48	7.98	7.55	1.81	0.77	6.57	2.37	1.41	7.27	2.96	1.95	1.24	3.27	1.32	0.00	3.05	1.49	0.00	0.00	2.69	1.58	1.16	4.94	5.52	3.62	5.19	10.47	3.23	1.09	5.51	4.25	3.13	2.69	15.25	12.13		
Diltiazem	0.68	2.78	3.11	1.30	1.19	3.13	0.81	0.28	2.58	1.61	0.94	0.54	1.72	0.57	0.24	1.96	1.39	1.68	1.60	2.78	0.50	0.33	1.60	2.03	2.84	2.87	7.52	1.96	0.36	2.75	2.27	1.73	1.84	7.19	5.25		
Dipyridamole	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.32	0.35	0.15	-	-	0.12	0.15	0.20	0.14	0.11	0.31	0.37		
Disopyramide	-	0.03	-	0.02	0.01	0.03	0.01	0.06	0.00	0.04	0.03	0.03	-	0.03	-	-	-	-	-	-	-	0.06	0.07	0.08	0.06	0.21	0.37	0.17	0.26	0.22	0.21	0.26	0.23	0.63	0.60		
Enrofloxacin	-	-	-	-	-	-	-	14.32	12.65	12.91	13.50	13.56	27.32	11.50	-	-	-	-	-	-	-	0.44	0.94	7.29	2.46	5.96	3.96	-	0.63	0.51	8.40	0.61	0.56	1.62	0.93		
Erythromycin	-	4.04	-	3.60	1.06	15.71	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.09	5.92	-	-	7.30	-	8.11	2.70	5.55	-	3.27	3.83	9.75	7.85		
Erythromycin-H2O	0.60	2.84	2.78	1.42	1.22	2.89	0.58	1.78	2.95	3.32	2.44	2.25	4.18	1.83	1.34	2.87	2.39	4.44	3.55	7.04	2.04	1.45	3.20	3.89	5.18	5.24	13.37	7.25	0.74	2.60	2.31	1.94	1.97	6.80	6.95		
Estradiol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
Estriol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
Estrone	0.84	0.47	0.67	0.25	0.33	0.67	0.44	0.46	0.55	0.59	0.40	0.37	0.47	0.34	0.21	0.33	0.36	0.27	0.35	0.71	0.22	0.11	0.15	0.22	0.24	0.16	0.54	0.14	0.10	0.27	0.25	0.22	0.15	0.50	0.22		
Ethenzamide	-	0.03	0.12	0.03	0.02	0.03	0.00	0.06	0.61	0.40	0.24	0.24	0.51	0.13	0.09	0.27	0.36	0.47	0.31	0.78	0.00	0.07	0.29	0.51	0.64	0.91	1.65	0.40	0.16	0.46	0.36	0.36	0.30	0.96	1.10		
Ethynylestradiol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
Fenoprofen	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.20	1.16	-	0.18	0.30	-	-	-	-	-		
Furosemide	0.30	5.27	3.15	0.00	0.00	0.00	0.32	-	3.48	0.87	-	-	-	-	-	-	-	-	-	-	-	-	2.11	1.37	1.73	-	1.23	-	0.62	1.90	0.98	-	-	3.30	2.36		
Griseofulvin	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
Ibuprofen	23.32	13.59	28.25	10.35	10.32	28.64	9.09	-	9.13	4.20	5.04	4.52	9.08	6.97	3.21	5.79	4.12	7.01	11.68	16.69	4.02	5.71	3.70	5.49	9.91	13.12	-	4.69	14.10	14.56	10.69	13.33	12.99	27.90	14.01		
Ifenprodil	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
Indometacin	0.26	0.35	-	0.12	0.09	0.29	0.07	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.50	2.35	0.56	2.67	2.38	0.76	0.34	0.40	0.49	-	0.22	1.06	-		
Isopropylantipyrine	0.45	1.24	1.39	0.90	0.74	1.15	0.10	0.41	1.18	1.83	1.61	1.58	2.57	0.18	0.34	1.12	1.69	3.61	3.36	5.20	0.46	-	0.47	1.52	2.39	2.28	5.87	1.00	0.32	0.70	1.16	0.84	0.80	1.75	2.01		
Ketoprofen	0.19	0.82	0.77	-	0.38	0.48	0.13	0.40	-	-	-	-	4.43	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.20	0.23	0.11	-	-	0.56		
Levofloxacin	4.91	5.02	4.72	2.20	2.02	7.93	1.33	4.03	8.71	6.28	3.90	4.51	18.65	5.84	3.71	2.21	2.65	3.06	2.82	5.14	5.43	1.67	5.24	2.33	2.77	3.39	17.01	6.36	1.37	4.67	2.36	2.35	2.88	21.87	10.71		
Lincomycin	0.63	4.30	2.73	0.99	1.16	2.89	4.29	0.93	7.83	8.67	6.86	7.08	13.22	2.40	0.58	5.93	5.59	9.94	9.07	15.75	3.86	0.47	2.89	7.82	13.36	10.93	30.92	6.58	0.96	10.20	11.61	9.86	9.17	28.64	24.60		
Mefenamic_acid	3.49	14.26	14.37	5.87	5.11	-	4.61	4.11	20.44	16.58	14.88	13.38	24.77	7.33	1.92	17.81	14.42	19.28	19.83	12.31	8.62	2.47	7.93	20.50	27.38	21.96	41.60	19.70	3.22	23.06	16.69	-	13.72	34.59	19.61		
Metoprolol	-	0.23	0.75	0.33	0.09	0.17	0.04	-	-	-	-	-	-	0.27	-	-	-	-	-	-	-	0.14	0.23	0.44	0.96	0.72	1.55	0.76	0.16	0.47	0.30	0.49	0.43	0.58	0.75		
Nalidixic_acid	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.77	1.69	2.01	-	-	0.20	0.28	-	0.36	-	0.40	-		
Naproxen	9.87	14.96	13.79	5.28	5.72	23.27	13.50	2.47	11.95	8.40	7.08	8.07	11.79	6.89	1.45	12.92	9.25	11.07	12.46	21.71	11.50	6.75	11.74	17.00	20.75	20.06	43.75	6.28	8.15	30.03	27.20	20.66	20.81	54.00	21.68		
Norfloxacin	-	-	-	-	-	-	-	2.22	1.43	1.77	1.12	2.03	3.36	2.44	-	-	-	-	-	-	-	0.26	0.99	4.75	1.68	5.22	3.69	-	0.22	-	-	-	-	0.88	-		
Oxytetracycline	-	-	0.16	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.42	-	-	-	-	-	-	-	-	-	-	-		
Pirenzepine	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.04	0.05	0.05	0.04	-	0.13	-		
Primidone	-	0.59	0.08	-	0.13	0.42	0.12	-	1.93	1.92	1.64	0.91	3.55	0.21	-	1.34	1.10	2.02	2.54	2.03	-	0.71	0.41	-	2.41	2.72	6.03	1.61	0.54	1.52	1.60	1.63	1.50	3.39	-		
Propranolol	0.31	2.97	2.63	0.94	0.90	2.10	0.76	0.37	2.04	1.59	0.86	0.63	2.47	0.79	0.11	1.98	1.57	1.44	0.88	2.51	1.10	0.15	2.46	2.56	2.56	2.73	8.51	3.06	0.26	3.14	2.34	1.83	1.47	6.72	5.80		
Roxithromycin	3.13	18.05	17.92	7.02	6.35	15.21	3.49	2.87	12.29	10.94	7.50	7.46	14.29	3.38	0.56	8.47	7.62	10.82	8.36	17.85	3.77	2.68	16.65	21.94	24.18	23.08	66.29	21.43	2.54	20.59	17.61	14.41	15.08	53.04	37.39		
Salbutamol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
Sulfadimethoxine	-	0.32	0.44	0.19	0.16	0.25	0.00	0.06	0.26	0.58	0.40	0.40	0.43	0.12	-	0.64	0.78	2.05	1.69	1.65	-	-	0.42	1.33	2.20	2.40	4.13	0.08	0.07	0.56	0.88	0.75	0.87	1.22	0.13		
Sulfadimidine	0.01	3.60	3.86	1.73	1.34	2.13	0.04	0.33	9.96	8.79	7.71	8.12	10.22	0.42	-	6.08	3.49	6.27	4.79	6.71	0.35	0.28	0.63	2.14	2.99	3.11	6.39	0.92	0.15	0.93	1.24	1.04	0.93	1.82	1.02		
Sulfamerazine	-	-	-	-	-	-	0.12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.57	-	-	-	-	-	-	-	-		
Sulfamethoxazole	4.46	22.01	24.32	11.38	11.53	20.90	3.14	2.98	17.65	20.47	20.76	19.46	34.09	3.94	1.71	14.55	13.90	24.22	27.49	44.71	4.74	3.45	9.41	15.94	24.36	24.01	61.08	15.92	3.92	13.13	14.88	13.11	13.26	34.89	14.64		
Sulfamonomethoxine	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.36	0.27	1.70	0.95	-	0.08	0.12	0.07	0.09	0.09	0.18	0.13		
Sulfapyridine	6.94	-	-	-	3.36	-	2.01	2.87	12.26	11.26	7.45	7.64	15.50	4.17	1.74	7.79	6.88	8.77	7.03	17.71	3.95	1.66	14.79	12.87	14.84	12.79	39.46	13.08	2.03	11.56	8.34	7.20	6.09	19.22	7.67		
Sulfathiazole	-	2.80	2.77	-	-	-	-	-	2.91	2.55	1.67	1.54	1.61	0.19	-	5.09	2.26	5.09	3.74	3.99	0.38	-	-	3.37	3.10	4.47	6.06	0.48	0.29	4.19	2.72	2.21	2.07	3.72	1.25		
Sulpiride	22.71	99.25	103.38	44.99	48.59	109.54	36.96	7.85	51.90	67.06	54.81	52.92	106.62	22.11	5.12	39.95	38.52	59.70	58.11	106.79	19.23	6.51	39.13	61.63	83.10	84.73	206.10	66.82	4.99	46.54	43.27	35.53	36.35	114.87	80.39		
Tetracycline	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.17	-	-	-	-	-	-	-	-	-	-	-		
Theophylline	14.79	14.36	16.07	8.27	7.97	16.37	7.11	8.46	11.07	10.88	8.99	9.55	16.23	9.90	4.72	11.78	10.73	19.54	19.66	31.74	6.37	6.46	7.42	14.67	21.65	19.42	40.28	13.50	10.65	11.04	11.37	11.82	13.24	27.27	18.51		
Thiamphenicol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
Tiamulin	0.19	0.54	0.41	0.18	0.21	-	0.09	0.11	1.20	0.73	0.50	0.31	0.24	0.04	0.03	0.21	0.14	0.25	0.15	0.17	-	0.06	0.19	0.62	0.84	0.70	1.16	0.15	0.04	3.85	2.61	2.32	2.10	3.27	0.21		
Triclocarban	2.05	1.87	2.60	1.07	1.04	-	1.12	-	-	2.59	1.31	1.70	-	-	1.22	-	-	-	-	-	-	0.57	1.07	0.92	1.27	0.99	2.77	1.97	1.49	-	0.86	-	-	-	2.04		
Triclosan	-	5.15	3.37	0.81	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3.42	2.53	-	-	-	-	-	-	-	-	-	-		
Trimethoprim	0.84	4.56	5.29	1.89	1.87	5.86	1.92	0.44	6.04	5.87	4.28	4.11	8.68	1.41	0.30	3.71	3.06	3.98	4.14	5.91	-	0.31	1.04	4.65	5.74	5.60	13.62	4.24	0.48	6.91	6.48	5.00	5.05	18.23	13.19		
Tylosin	0.50	0.57	0.59	-	-	-	0.31	0.00	0.31	0.24	-	-	0.22	0.00	0.04	0.17	0.07	-	-	-	-	-	0.12	0.15	0.18	0.18	0.39	0.21	0.12	0.24	0.26	0.16	-	1.01	1.02		

Appendix D. Water Quality Impact of a Sewage Treatment Plant Damaged by Flooding Disaster on the Gyeongan River, Korea

D.1 Introduction

Pharmaceuticals and personal care products (PPCPs) are an important matter chiefly used for preventing disease and treating human and animals (S. Jobling. et al., 1998; Muckter et al., 2006; Triebskorn et al., 2007). From an environmental perspective, however, they implicate potential problems as pollutants that can have negative effects (Triebskorn et al., 2007). Despite many benefits we obtain from using PPCPs, effects of their remnants after such use on the environment are not currently taken into adequate consideration (Mompelat et al., 2009). In fact, there is a continued possibility brought up for PPCPs and estrogens to contaminate the environment and cause harm to ecosystem (N. Ratola et al., 2012; S.K. Behera et al., 2011; M.J. Gomez et al., 2007). Such PPCPs and estrogens influent to stream and river through sewage treatment plants (STPs) are influencing the ecosystem (Sheyla et al., 2013; Sandeep and Andrew, 2013). The STPs are an important facility that treats wastewater, night soil used by human and animals, while such wastewater contains PPCPs and endocrine disrupting compounds (EDCs) besides diverse materials (A.Y.C. Lin et al., 2008). These important STPs can lose the whole or part of its function for the reason of earthquake, fire or flooding. Then diverse pollutants would flow into a stream or river to affect the ecosystem (William, 2005), which would last until the function of STPs restore. In the summer of 2011, it happened that two important STPs at Gyeongan River were flooded. Because of inundation, untreated wastewater was discharged as a whole into the river causing its contamination. The present study dwells on the problems of PPCPs, estrogens and other pollutants when these STPs lost their functions by the flooding. Research was made on the toxicity occurring from PPCPs and estrogens introduced in the river with analysis on PPCPs and estrogens existing in the river after the accident. It is also going to consider whether proper countermeasure was made for the accident of flooding and how we could respond better.

D.2 Materials and methods

D.2.1 Gyeongan River

Gyeongan River is located in Gyeonggi province, southeast of Seoul, Korea, and it flows into the Han River. This River is an important drinking water source for populations in Seoul and metropolitan area. Gyeona River basin is covered by 60% forest, 16.7% agricultural and 2.6% livestock farms (2009). In addition, two livestock wastewater treatment plants are located upstream and middle stream.

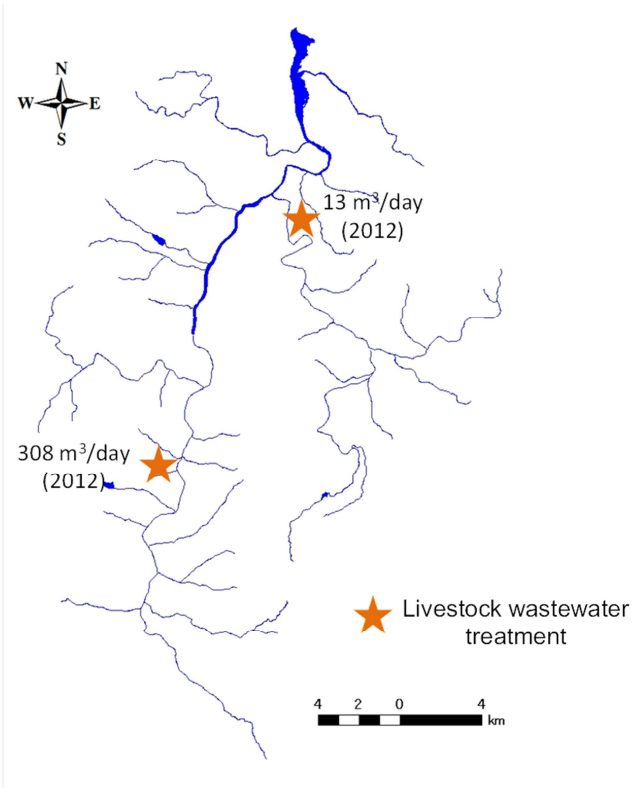

Figure D.1 Map showing livestock wastewater treatment locations

D.2.2 Accident description

Point A-1 is the mainstream of Geongan River while point B-1 is an affluent to Gyeongan River. Point C-1 is the region of combining point A-1, point B-1, and the effluent of STP-E. On Gyeongan River there are two livestock wastewater treatment plants. One of them is using STP-H to treat of the livestock wastewater as well as wastewater (Figure D.2).

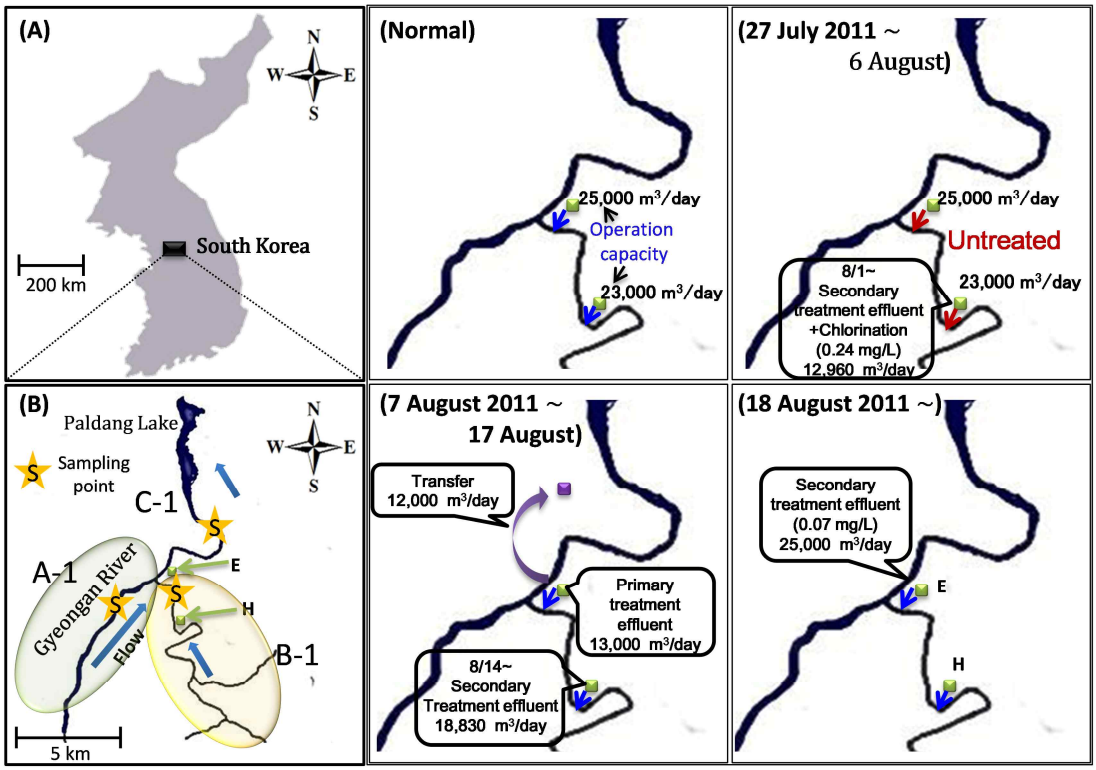

Figure D.2 River map of Gyeongan River and accident region and typical change of STPs by response to accident

On July 27, 2011, there was a torrential rain bringing on the flooding of STP E and H upstream from point B-1 and point C-1, respectively, which directly caused untreated wastewater to flow in the river. H STP was temporarily restored on August 1, and after chlorine disinfection (0.24 mg/L) of the secondary effluent, it treated the wastewater of 12,960 m^3/day. STP-E was temporarily restored on August 7 and the first line of STP-E (13,000 m^3/day) was discharged into the river through chlorination of the primary settling tank, bioreactor and secondary settling tank, while the second line (12,000 m^3/day) and excretions were transported to another treatment plant for treatment. On August 18, the second system was also restored and STP-E came to treat a total wastewater of 25,000 m^3/day. While the flooding set an exceptional term of water quality standards for effluents of STPs (July 27 to Sep 30, 2011), Gyeongan River brining in the effluent was put to fast restoration to minimize contamination since it was an important source for people in Seoul and the Metropolitan area to use.

D.2.3 Countermeasure and restoration

STP-E was completely flooded with damage to flow meter, pump, electrical facilities and especially bioreactor was submerged to let lose all the microbes. Since it took much time to culture microbes, STP-E moved the microorganisms from the bioreactor of another STP as a means to fast restoration. As a result, the function of bioreactor recovered in a short time to allow treating the wastewater. For damaged electrical facilities, simple generator was first used for pump and aeration.

STP-H was only partially inundated for grit chamber, influent pump and UV disinfection equipment without damage to other facilities including electricity. This enabled restoration in a shorter time than STP-E, bringing back to normalcy of all the facilities from August 14 except bio film filtration and UV disinfection.

D.2.4 Sampling of PPCPs and estrogens

Primary survey on PPCPs and estrogens were made in October 2010, ten months before the accident, and another survey of the river was conducted at the end of August 2011, one month after the accident happened. Right after the flooding, there was a problem with sampling due to much rain and flood of the river. Then in November, three months later, another survey was conducted and the final survey was carried out in January 2012.

D.3 Results and discussion

D.3.1 Flow and Rainfall

The rain starting in July 2011 turned to torrents at the end of the month (Figure D.3). This increased the flow rate of the river rapidly causing STP to be submerged in the accident. On the inundated area fell a heavy rain maximum at 249 mm/sec recording a maximum flow rate of 1185 m^3/sec at Gyeongan River. Though seasonally Korea has much rain in the summer (July through September), this accident unusually happened too much rain fell momentarily and caused the river a rapid increase in the flow rate submerging STPs. In case of such an accident, it will fail or lower the function of STPs and takes much time with restoration of the facilities. Besides, the untreated wastewater will leak out into the river giving harm to both an ecosystem and the people who use the river water.

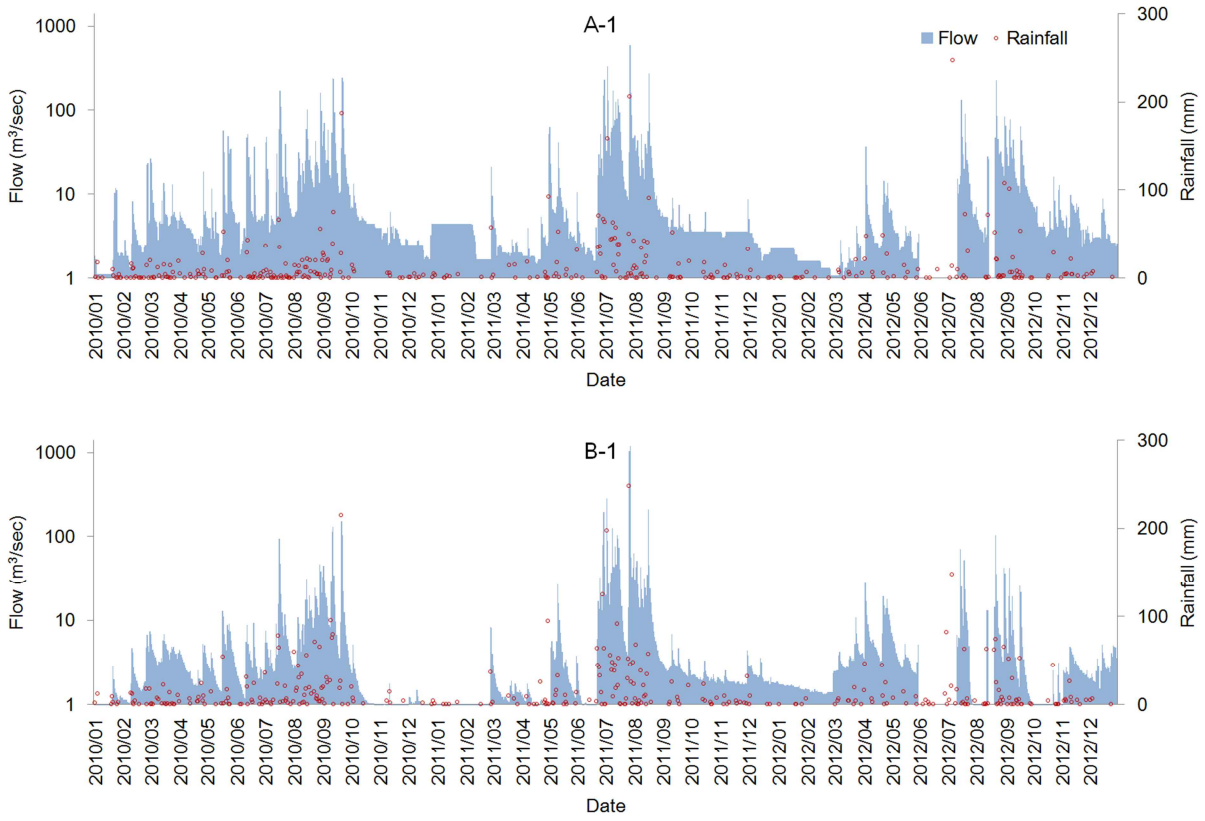

Figure D.3 Change in flow rate and precipitation of Gyeongan River (A-1 and B-1) from Jan 2010 through Dec 2012

D.3.2 Water quality in STPs

D.3.2.1. Influent of E STP

Figure D.4 shows the BOD, COD_{mn}, T-N and total coliform for the influent and effluent of STP from the July through the end of September, 2011. There was no data of water quality found from July 27, which was the day when the accident first occurred, through August 6, and the wastewater coming in with rainwater was totally discharged into the river. Due to the restoration of accident, E STP's experimental results on the influent and effluent exist only partially with normal daily ones appearing from the date of September 16. Most results of experiment showed little difference from before occurrence of the accident, which is considered due to dilution caused by the rain. Exact verification was impossible because the flow meter became under water when the accident did happen.

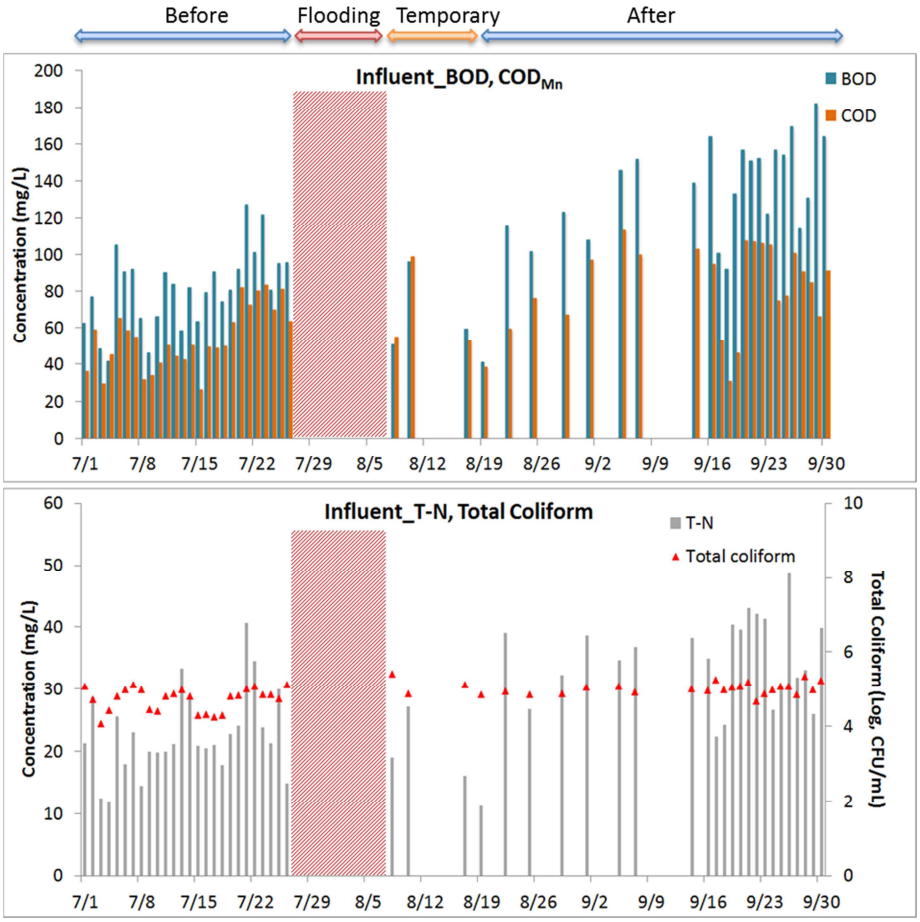

Figure D.4 Change of BOD, COD_{mn}, T-N and total coliform in the influent of STP-E before and after accident

D.3.2.2. Influent of H STP

On the other hand, at the STP-H with a partial flooding of grit chamber, inflow pumping plant and UV disinfection equipment, faster restoration was possible compared to STP-E. Similar to STP-E, there was no experimental result found and all was literally discharged into the river. Though BOD and COD_{mn} decreased after August 7, when wastewater treatment started from temporary restoration, BOD for inflow showed increase in concentration after September. T-N showed the same tendency as BOD, which is considered because decreasing rain caused decrease of the influent in dilution ratio, increasing the concentration.

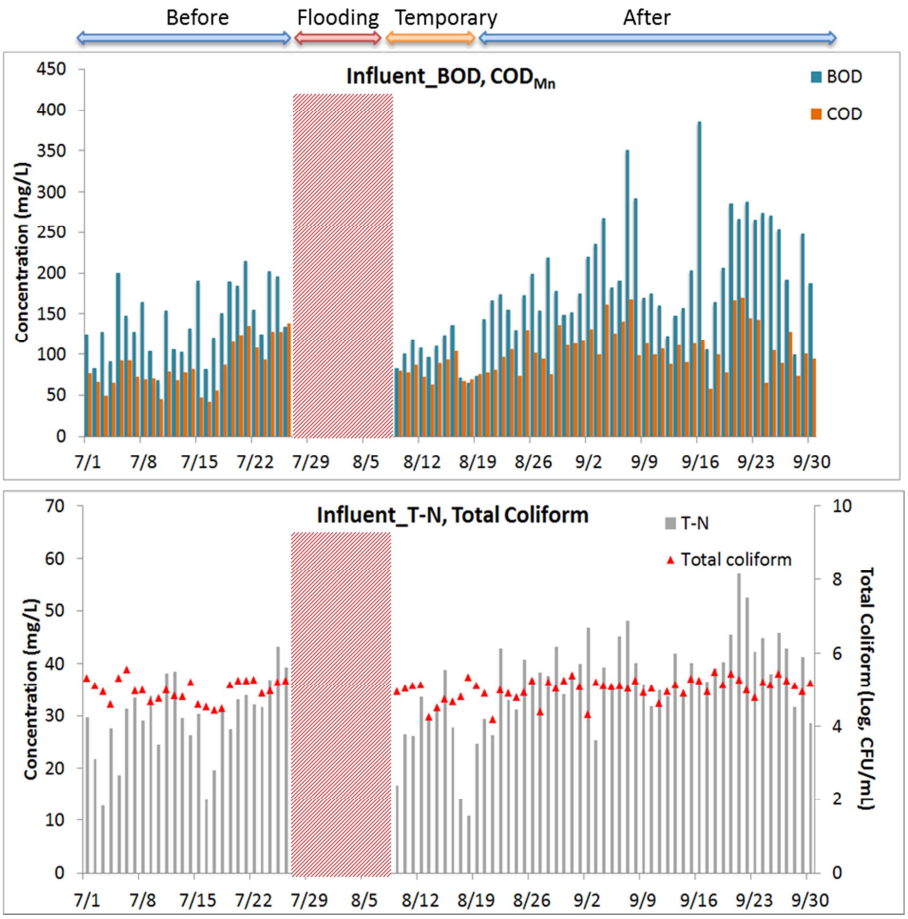

Figure D.5 Change of BOD, COD_{mn}, T-N and total coliform in the influent of STP-H before and after accident

D.3.2.3. Effluent of STP E and H

In Korea, the standard values provides that the effluent of the STPs be under 10 mg/L for BOD and 40 mg/L for COD_{mn} in water quality (Jan. 2011). From Aug 6, the data showed that STP-E had BOD and COD_{mn} values lower than the standards of water quality, while T-N values were also lower than the standard of 20 mg/L though higher than before. The standard for total coliform of the effluent is 1,000 CFU/mL, but detection showed many cases of concentration being higher than before the accident, though lower than the water quality standards. From August 8 when it was reported to pass the water quality standard for effluent, however, all items turned out to meet the water quality standards. Still, if chlorination had been executed with a higher concentration than 0.07 mg/L, it would have been possible to treat total coliform more properly in more safety. For the effluent of STP-H, all of BOD, COD_{mn} and total coliform showed increase after the accident. However, all items showed lower values than the standard water quality. While T-N showed the same concentration as before the accident, BOD, COD_{mn} and total coliform showed a lower concentration. BOD and COD_{mn} are considered to have appeared higher in effluents too as the

influent increased, while total coliform was detected to be a little higher than the existing concentration because of the problem in the process of UV disinfection.

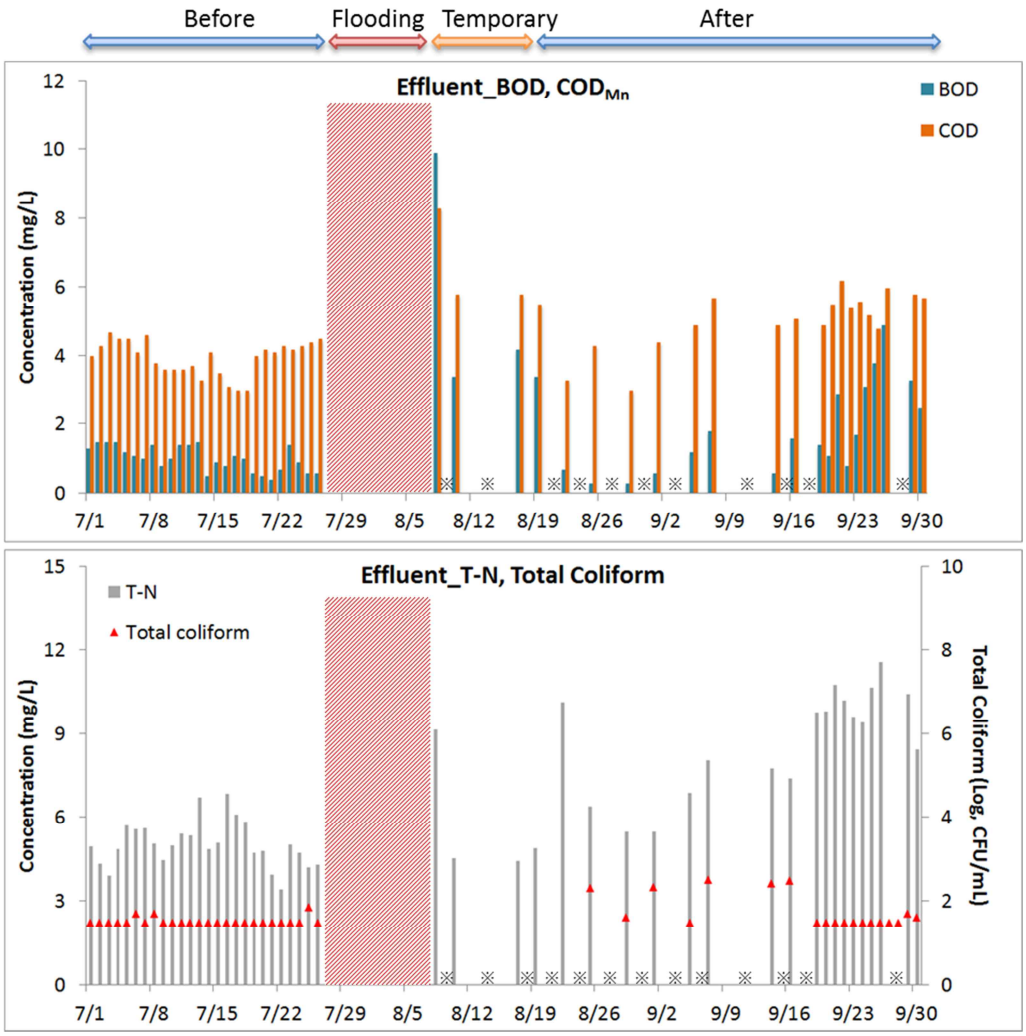

Figure D.6 Change of BOD, COD_{mn}, T-N and total coliform in the effluent of STP-E before and after accident

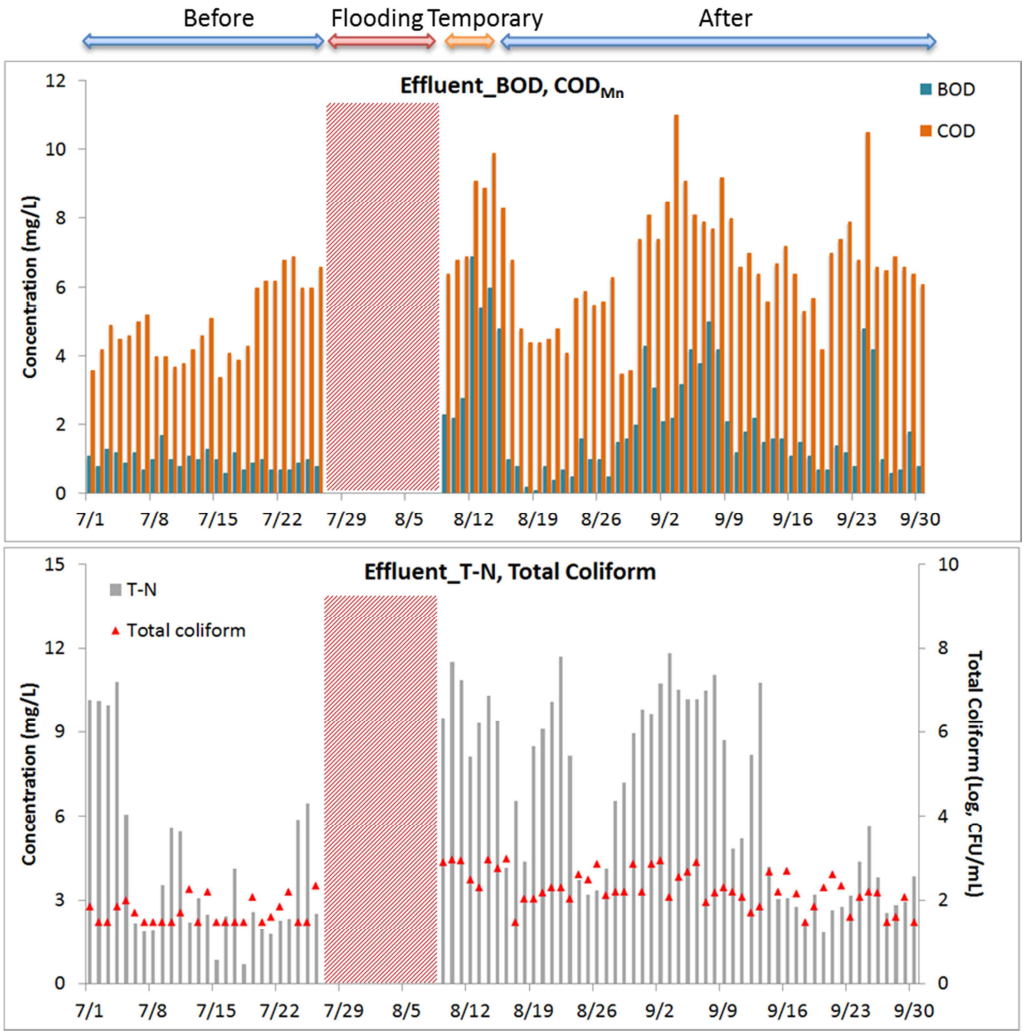

Figure D.7 Change of BOD, COD_{mn}, T-N and total coliform in the effluent of STP-H before and after accident

D.3.3 Water quality in river

In July and August when the accident happened, the river showed very low BOD, COD_{mn}, T-N and T-P (Figure D.8).

Figure D.8 Water quality of BOD, COD_{mn}, T-N and T-P in points A-1, B-1 and C-1

Point A-1 in no relation to the accident showed a BOD concentration of 5.4 mg/L in June but a low concentration under 0.8 mg/L from July due to dilution. Other items also showed a lower concentration in July and August compared to June. For point B-1 and C-1 affected by the flooding of STPs, they showed decrease in BOD and CODmn in July compared to June, while other items all showed a tendency of increase. This is considered a result of increase caused by influent as the function of STPs lowered. Despite the low concentration of detection caused by dilution with a rapid increase in the flow of the river, increase of all the items except BOD and CODmn is considered to indicate a very large volume of pollutants leaked out in the river.

Table D.1 Present condition of water quality at points A-1, B-1 and C-1

	A-1						B-1						C-1					(mg/L)
	BOD	COD	T-N	NH3-N	NO3-N	T-P	BOD	COD	T-N	NH3-N	NO3-N	T-P	BOD	COD	T-N	NH3-N	NO3-N	T-P
2010/01	1.60	5.30	8.66	1.13	6.81	0.41	3.10	5.50	8.76	5.01	2.64	0.04	3.10	6.40	8.49	2.46	5.79	0.30
2010/02	5.80	11.00	6.12	1.91	3.81	0.37	1.40	3.80	6.23	3.36	2.41	0.07	3.40	7.40	7.43	2.08	4.69	0.26
2010/03	1.90	5.20	4.77	0.63	4.13	0.16	1.40	2.90	5.11	0.59	3.51	0.02	2.90	5.20	5.37	0.71	4.29	0.12
2010/04	2.20	5.70	4.76	0.21	3.88	0.20	3.10	3.80	4.51	0.73	2.86	0.08	3.80	6.20	5.15	0.55	3.77	0.18
2010/05	9.90	9.00	3.53	0.07	2.33	0.22	4.80	4.10	3.78	0.66	1.30	0.11	8.50	8.80	3.73	0.22	2.66	0.17
2010/06	7.60	11.20	2.87	0.04	1.95	0.17	2.60	3.50	3.94	0.63	1.62	0.04	4.20	7.50	3.08	0.13	2.56	0.19
2010/07	7.40	10.80	3.74	0.05	2.90	0.21	1.90	3.70	2.61	0.08	1.75	0.06	2.50	5.30	3.80	0.10	3.10	0.13
2010/08	1.50	4.00	3.16	0.13	2.90	0.17	1.30	3.70	3.12	0.15	2.15	0.11	2.50	6.20	3.28	0.12	2.76	0.17
2010/09	1.00	3.60	3.71	0.10	3.35	0.07	1.40	4.30	3.01	0.13	2.06	0.12	2.00	5.30	3.48	0.15	2.82	0.17
2010/10	1.50	4.50	5.30	0.06	4.66	0.23	0.90	2.40	3.73	0.17	2.29	0.08	1.10	4.20	4.28	0.03	3.61	0.08
2010/11	2.30	5.80	6.64	0.93	4.29	0.16	1.30	3.30	3.78	0.02	2.04	0.03	1.30	3.70	4.57	0.47	2.34	0.09
2010/12	0.90	2.90	9.38	0.60	7.55	0.18	0.70	4.10	4.41	0.08	1.38	0.03	1.20	3.90	7.17	0.27	6.43	0.12
2011/01	1.50	5.40	11.40	0.36	8.67	0.29	2.00	5.90	7.49	3.24	1.38	0.49	1.20	5.40	9.97	2.21	6.58	0.19
2011/02	1.70	4.80	9.42	2.14	6.98	0.22	3.20	5.70	10.67	4.78	2.83	0.10	1.50	6.30	9.35	2.42	5.03	0.14
2011/03	1.50	4.80	7.01	0.92	5.48	0.19	1.60	5.90	5.97	1.65	3.67	0.05	2.10	5.90	6.66	0.51	5.15	0.13
2011/04	4.50	8.10	5.90	0.41	5.09	0.21	2.00	5.10	4.56	0.19	3.17	0.10	4.40	9.10	4.32	0.18	3.57	0.13
2011/05	1.40	3.90	5.54	0.14	5.35	0.10	1.20	3.10	5.16	0.10	4.15	0.07	1.40	4.30	4.63	0.17	4.23	0.11
2011/06	5.40	8.20	3.99	0.17	3.06	0.17	1.80	8.80	2.68	0.04	1.62	0.04	4.20	8.40	3.23	0.05	2.49	0.13
2011/07	0.80	5.40	3.20	0.09	2.33	0.10	0.80	2.80	3.94	0.40	2.35	0.07	1.20	3.90	3.61	0.10	3.00	0.16
2011/08	0.50	4.80	2.80	0.12	2.36	0.19	0.60	2.40	3.26	0.65	2.30	0.04	1.00	4.10	2.90	0.15	2.35	0.09
2011/09	3.60	6.40	3.49	0.01	2.69	0.07	1.40	4.20	4.62	0.30	1.75	0.15	2.20	6.60	3.42	0.03	2.59	0.08
2011/10	1.80	5.10	4.57	0.01	3.53	0.27	1.20	3.70	2.63	0.04	1.49	0.04	2.00	5.10	4.46	0.07	3.15	0.17
2011/11	1.20	4.70	4.48	0.11	3.59	0.22	1.40	5.50	3.20	0.14	3.06	0.03	1.90	5.10	4.33	0.12	3.59	0.11
2011/12	1.10	4.20	4.98	0.26	4.12	0.10	2.70	4.10	4.78	0.25	4.25	0.07	1.10	4.50	6.14	0.28	5.19	0.06
2012/01	1.50	4.30	8.54	0.92	7.33	0.08	0.60	6.90	7.87	1.31	5.37	0.05	1.60	5.50	8.80	2.29	6.23	0.07
2012/02	1.50	5.20	10.12	4.01	5.84	0.06	1.60	5.40	6.17	1.25	3.81	0.06	2.20	5.90	9.36	4.12	4.93	0.05
2012/03	5.40	8.40	9.06	3.69	3.95	0.08	2.30	5.80	7.00	2.79	2.84	0.06	4.30	7.40	7.35	2.82	3.41	0.05
2012/04	6.80	8.70	5.38	1.33	3.55	0.08	2.10	3.20	4.61	0.23	3.41	0.03	3.60	6.40	4.52	0.47	3.47	0.04
2012/05	2.10	5.30	3.08	0.09	2.48	0.03	2.80	4.90	4.48	1.01	2.51	0.06	3.40	6.70	2.45	0.12	1.79	0.03
2012/06	6.90	11.40	1.91	0.03	1.28	0.06	3.40	5.00	3.10	0.58	1.47	0.10	5.70	11.70	2.07	0.05	1.34	0.02
2012/07	3.70	7.60	1.82	0.11	1.46	0.06	1.90	4.70	4.81	0.53	1.77	0.18	1.70	4.80	3.10	0.21	2.29	0.06
2012/08	3.90	8.00	2.02	0.04	1.46	0.02	1.20	4.20	4.06	0.33	2.78	0.10	2.30	5.60	2.50	0.14	1.71	0.08
2012/09	0.80	2.80	3.02	0.10	2.34	0.07	0.50	2.30	2.77	0.08	2.53	0.05	1.10	3.10	2.87	0.09	2.33	0.04
2012/10	1.20	4.70	5.87	0.48	4.83	0.04	1.00	3.20	3.04	0.05	2.25	0.04	1.20	4.50	3.35	0.07	2.94	0.04
2012/11	3.10	4.00	3.40	0.73	2.28	0.04	0.50	2.20	2.62	0.05	2.09	0.04	1.80	3.80	3.91	0.44	3.04	0.05
2012/12	1.20	3.60	7.66	1.71	5.64	0.04	1.00	3.40	4.67	0.27	3.26	0.03	1.70	3.90	6.28	1.16	4.80	0.05
2013/01	1.50	3.70	7.49	1.92	5.16	0.07	2.90	5.40	6.41	3.63	2.51	0.09	4.30	5.50	6.24	2.10	3.87	0.08

D.3.4 Coliforms in river

Table D.2 shows the Korean standards of rivers. It requires that total coliforms in Ia class should be detected under 0.5 CFU/mL and fecal coliform under 0.01 CFU/mL. For grade III and under, total coliforms should be detected under 50 CFU/mL and fecal coliforms under 10 CFU/mL.

Table D.2 Standards of water quality for rivers of Korea

Grade	pH	BOD (mg/L)	COD_{mn} (mg/L)	SS (mg/L)	DO (mg/L)	T-P (mg/L)	Coliform group (CFU/mL)	
							Total coliform	Fecal coliform
Ia	6.5~8.5	under 1	under 2	under 25	more than 7.5	under 0.02	under 0.5	under 0.01
Ib	6.5~8.5	under 2	under 4	under 25	more than 5.0	under 0.04	under 5	under 1
II	6.5~8.5	under 3	under 5	under 25	more than 5.0	under 0.1	under ,0	under 2
III	6.5~8.5	under 5	under 7	under 25	more than 5.0	under 0.2	under 50	under 10
IV	6.0~8.5	under 8	under 9	under 100	more than 2.0	under 0.3	-	-
V	6.0~8.5	under 10	under 11	-	more than 2.0	under 0.5	-	-
VI	-	10 ~	11 ~	-	~ 2.0	0.5 ~	-	-

Though total coliforms in Gyeongan River tend to increase in the summer, after the accident of 2011, total coliforms and fecal coliforms have increased rapidly. Point A-1, which is an upper stream than this accident of flooding, seems to have increased in concentration than usual because of the influent pollutants caused by the torrential rain. For point B-1 and C-1, however, with functional loss of the STP, untreated wastewater was influent as a whole resulting in very high concentrations detected. Point B-1, which showed fecal coliforms of 70 CFU/mL and total coliforms of 170 CFU/mL in July 2011, showed fecal coliforms of 240 CFU/mL and total coliforms of 350 CFU/mL in August after the accident, proving to have increased over twice. From point C-1, fecal coliforms were detected at 502 CFU/mL and total coliforms at 964 CFU/mL. Concentration in fecal coliforms rather decreased in August after the accident because, together with increase of flow rate, STP-E had disposed of execrations by moving them to another place.

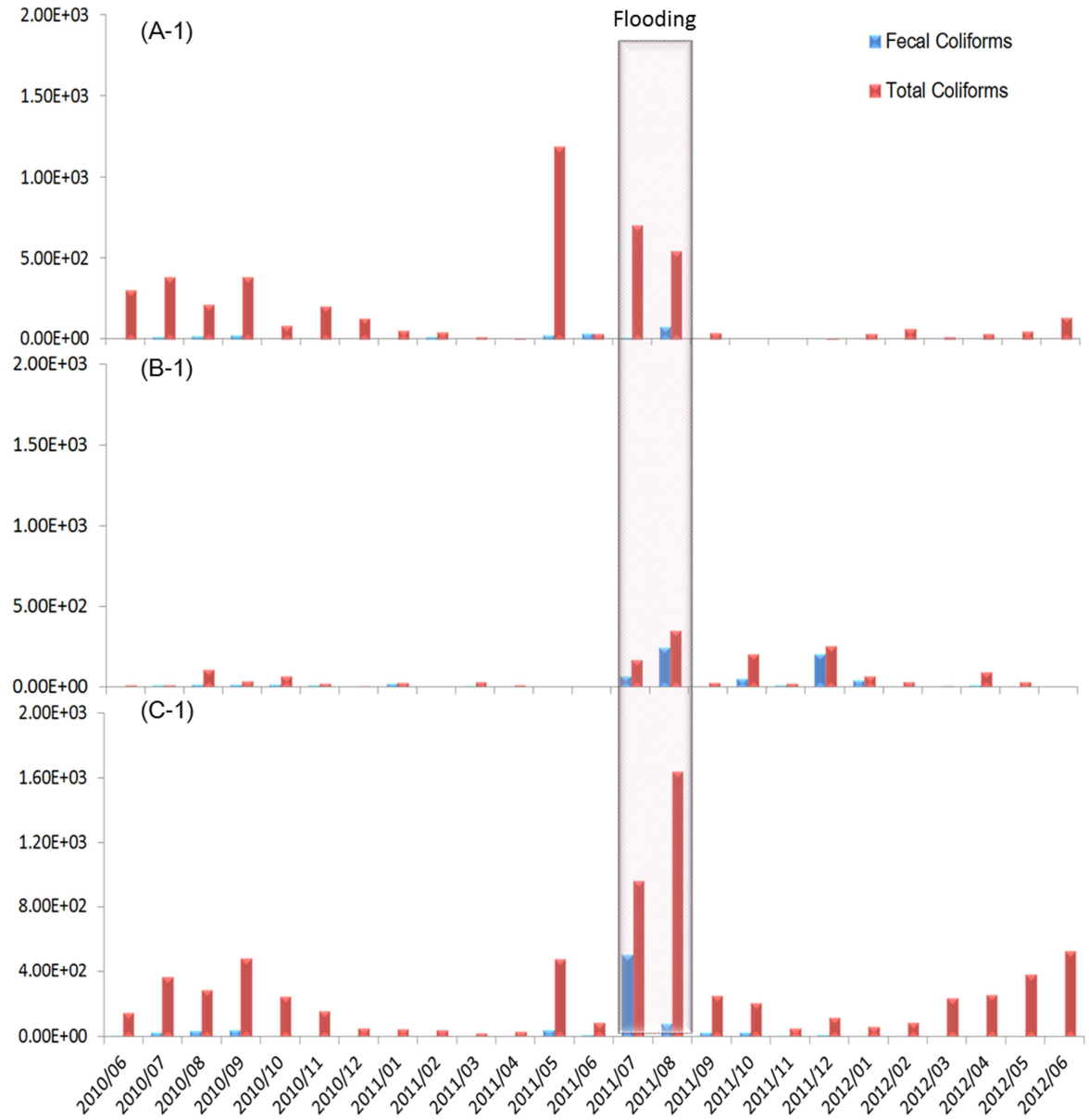

Figure D.9 Change of fecal, total coliforms at A-1, B-1 and C-1 points from June 2010 through June 2012

D.3.5 PPCPs and estrogens in river

Sampling was executed at the river before and after the accident, which was ten months before, and on August 29, 22 days after the restoration of STPs functions. Then, three and six months after the accident, sampling was conducted at the same point. Reportedly, 12 days after the accident, the functions of STPs were restored to normal, but one month after the accident there still was a relatively high detection of PPCPs and estrogens in the river.

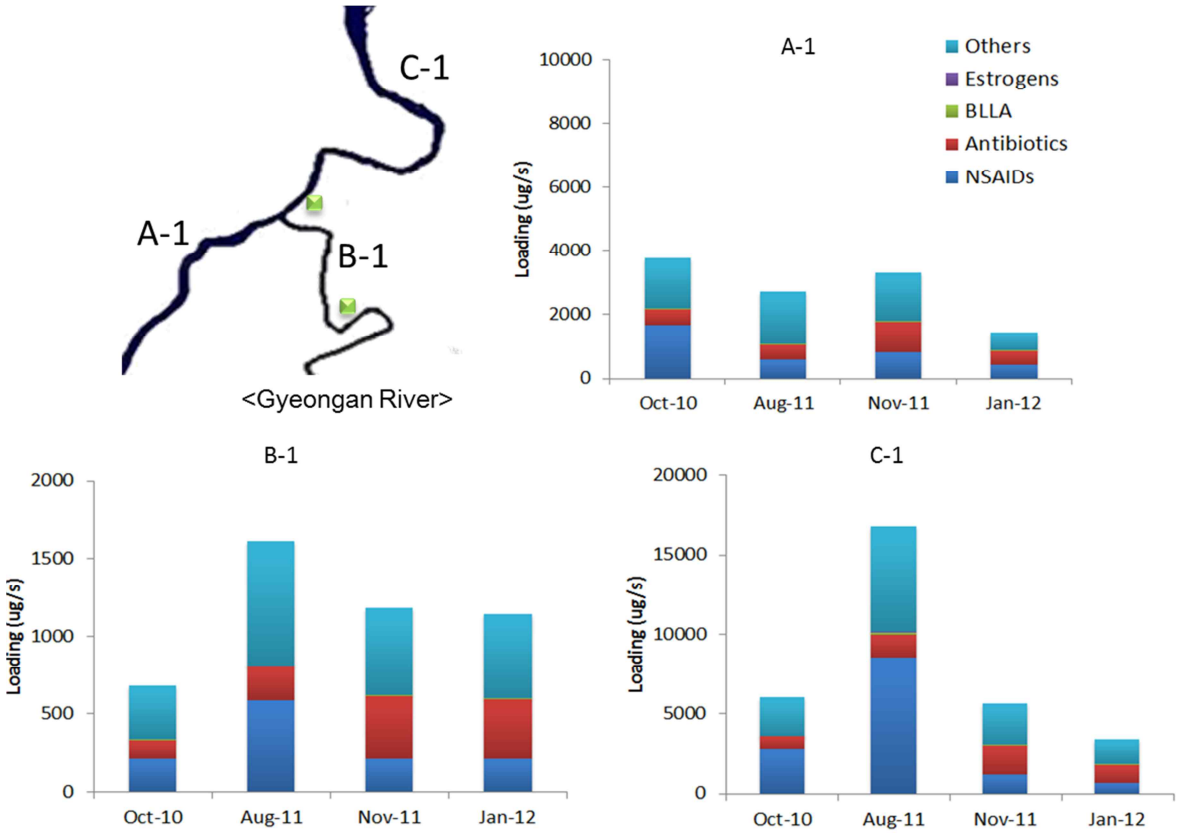

Figure D.10 Change of NSAIDs, antibiotics, BLLAs and estrogens detected in Oct 2010 (1 month before accident), August (1 month after), November 2011 and Jan 2012

At point C-1 with inflow of STP's effluent, all compounds including non-steroidal anti-inflammatory pharmaceuticals (NSAIDs), antibiotics, blood lipid-lowering agents (BLLAs), estrogens had increased. For August 2011, there is a cause to convince that PPCPs and estrogens detected from the river have been introduced from STPs. Accordingly, Figure D.11 shows kinds of PPCPs and estrogens detected from points B-1 and C-1.

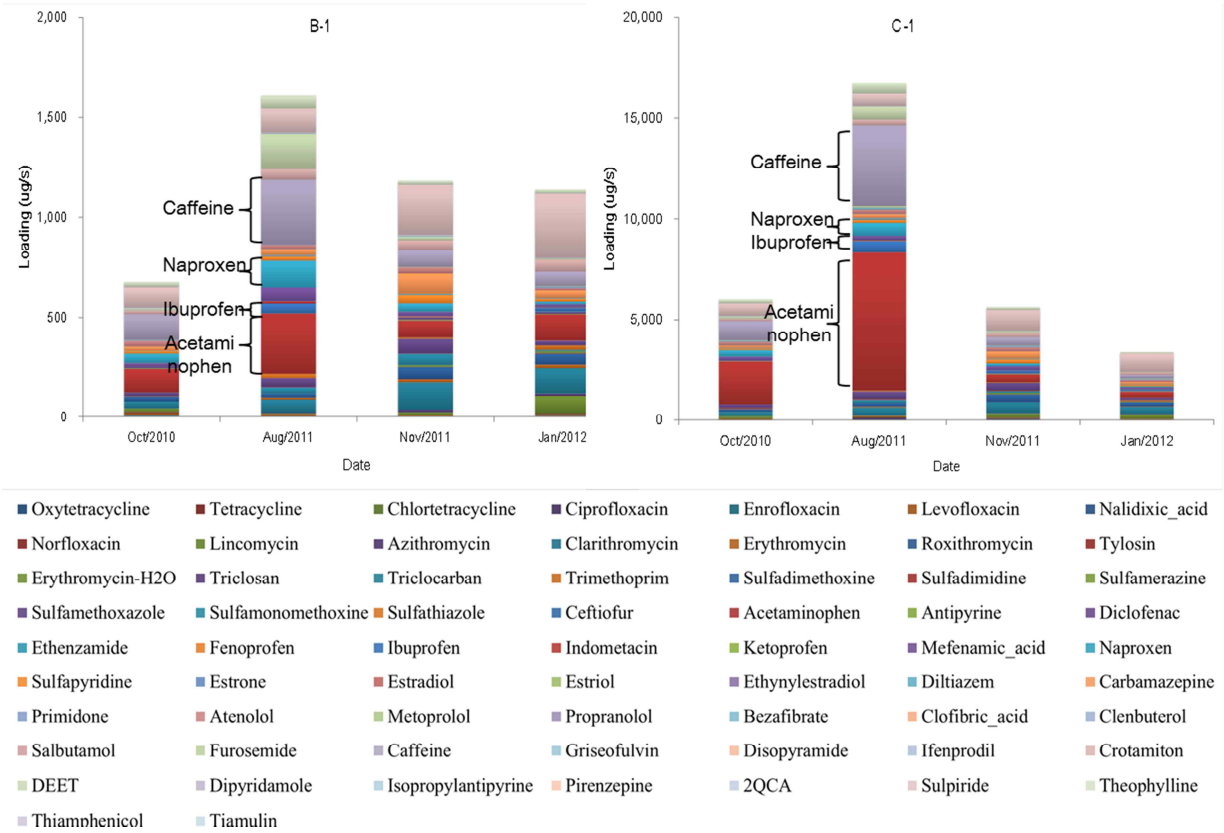

Figure D.11 PPCPs and estrogens mainly detected from point B-1 and C-1 due to the accident

From B-1 and C-1 points, acetaminophen, caffeine, ibuprofen and naproxen were chiefly detected. Though acetaminophen, caffeine, ibuprofen and naproxen are compounds with a high removal at the STPs, they are also matters with lots of inflow being detected from the river with a high concentration. In August 2011, PPCPs and estrogens increased much at point B-1 and C-1, it is considered to have come in from the STPs. However, it was impossible to verify exactly whether all the PPCPs and estrogens had flowed in from the STPs or how much of them had come in. It was because the STPs went through the process of restoration, which made the sampling of influent and effluent difficult. However, though just one month passed after the occurrence of accident, PPCPs and estrogens detected from the river showed a very high concentration (Nov. 2011). PPCPs and estrogens leaked out can affect humans who continue to use an ecosystem and the river as a source.

D.3.6 Toxicity of PPCPs

PPCPs existing in the water are known to make a harmful effect on aquatic ecosystem and they infiltrate in the body of living organism to affect the ecosystem and human health seriously (Pal, A. et al., 2010). Reported typical influence includes decreased number of individuals, lowered virility, carcinogenicity, reduced immunity. That's why methods to evaluate ecological toxicity are under development with toxic experiment carried out basically using the aquatic creatures such as water

flea, fish, algae with lots of researches related to PPCPs. Table D.3 shows the diverse toxic results from PPCPs remaining water.

Table D.3 Toxicity data of PPCPs

Compounds	Taxon	Species	Test*	Acute toxicity		Reference
Chlortetracycline	Crustacean	Magna	EC_{50}	225 mg/L	-	Park S. et al., 2008
	Fish	Latipes	EC_{50}	78.9 mg/L	-	
	Plant	Gibba	growth NOEC	0.1 mg/L	-	
Diclofenac	Crustacean	Magna	EC_{50}	22.43 mg/L	-	Park S. et al., 2008 Ferrari et al., 2003
	Crustacean	Dubia	NOEC	1 mg/L	-	
	Fish	Latipes	Egg fertility NOEC	1 mg/L	-	
Erythromycin	Crustacean	Magna	EC_{50}	210.6 mg/L	-	Cleuvers, M. 2003
	Algae	Subspicatus	growth NOEC	0.0103 mg/L	-	
	Algae	leopoldensis	growth NOEC	0.002 mg/L	-	
Ibuprofen	Algae	Subspicatus	EC_{50}	315, 342.2 mg/L	growth inhibition	Cleuvers, M. 2004
	Crustacean	Magna	EC_{50}	1~100, 101.2, 108 mg/L	immobilization	
	Mollusc	Carinatus	LC_{50}	17.1 mg/L	survival	
	Fish	Latipes	LC_{50}	>100 mg/L	mortality	
Mefenamic acid	Crustacean	Platyurus	LC_{50}	3.95 mg/L	mortality	Kim, J. W. et al., 2009 Pounds N. et al., 2008
	Fish	Latipes	LC_{50}	8.04 mg/L	mortality	
Naproxen	Algae	Subspicatus	EC_{50}	31.82 mg/L	growth inhibition	Cleuvers, M. 2003 Isidori M. et al., 2005
	Rotifer	Calyciflorus	EC_{50}	0.56 mg/L	growth inhibition	
	Crustacean	Magna	EC_{50}	66.37 mg/L	immobilization	
	Cnidarian	Attenuate	LC_{50}	22.36 mg/L	mortality	
	Cnidarian	Attenuate	EC_{50}	2.62 mg/L	mortality	
	Crustacean	Magna	growh NOEC	10 mg/L	-	
	Crustacean	Macrocopa	Reproduction NOEC	0.37 mg/L	-	
Oxytetracycline	Crustacean	Magna	EC_{50}	621.2 mg/L	-	Cleuvers, M. 2003 Cleuvers M. 2004 Isidori M. et al., 2005
	Fish	Latipes	LC_{50}	110.1 mg/L	-	
	Crustacean	Magna	EC_{10}	7.4 mg/L	-	
	Algae	Subspicatus	growth NOEC	0.183 mg/L	-	
	Algae	Cylindrica	growth NOEC	0.0031 mg/L	-	
Sulfathiazole	Crustacean	Magna	EC_{50}	149 mg/L	-	Isidori M. et al., 2005
	Crustacean	Magna	Reproduction NOEC	2.22 mg/L	-	
	Fish	Latipes	EC_{50}	>500 mg/L	-	

*EC_{50} : half effective concentration, LC_{50} : half lethal concentration, IC_{50} : half inhibitory concentration, NOEC: no observed effect concentration

Chlortetracycline, diclofenac, erythromycin, ibuprofen, mefenamic acid, naproxen, oxytetracycline, and sulfathiazole detected from Gyeongan River showed very low concentrations in toxicity compared to those known. However, it is not a fact that there is no problem when accident happens at a STP and untreated PPCPs and estrogens are introduced to the river. The problem is that there are still limitations in the research of toxicity on PPCPs and estrogens and many are short-term studies. Though concentration of PPCPs and estrogens detected from Gyeongan River exists by the unit of ng or μg for L, this may make a long-term effect on aquatic life and we need diverse researches on toxicity.

D.4 Conclusions

There was an accident in which flooding of STPs at Gyeongan River discharged untreated wastewater into the river. Since it is the river influent to a source, many efforts were made to restore the STPs. The biggest matter involved in the restoration was the loss of microbes in the bioreactor. Fast restoration was only made possible by carrying in microorganisms of another STP as it was. After the occurrence of accident, this plant was set with an exceptional term for water quality standards of effluent while at the STPs after temporary restoration effluent proved to be suitable for the standards. Compared to before the accident, however, BOD, COD_{mn} and total coliform increased in concentration, while STP-H produced a higher detection of total coliform from the loss of UV disinfection process. Though at Gyeongan River, BOD and COD_{mn} had decreased in concentration by dilution from the heavy rain, T-N, NH_3-N, NO_3-N and T-P still increased in concentration despite the dilution. Besides, in the region of effluent from the STPs after the accident, there was much increase in the concentration of total coliform and fecal coliform. Since coliform can be removed a lot by chlorination, such an accident calls for proper disinfection by means of this kind. Lastly, one month after the accident, PPCPs and estrogens in the river showed a higher concentration than detected before. At point C-1 with the effluent of the STP, all matters increased including NSAIDs, antibiotics, BLLAs and estrogens. Especially acetaminophen, caffeine, ibuprofen and naproxen increased in concentration, which are the substances reported to be with high removals at the STPs. True that the concentration existing in the river is much lower than the reported toxicity of PPCPs, but they still may harm the aquatic ecosystem and humans with their long-term influence, which necessitates research on this subject. At STPs, loss or reduction of its function causes diverse pollutants to flow in the river. In this study, BOD, COD_{mn} and T-N revealed no problem with the water quality standards and total coliforms also showed no problem either regarding effluent, which could be managed even better by proper disinfection. Nonetheless, PPCPs and estrogens showed a high concentration even one month after the occurrence of accident, which may affect the ecosystem on a long-term basis. In case of problems occurring with the function of STPs, we must remember that research is also needed for the management of trace compound such as PPCPs and estrogens.

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